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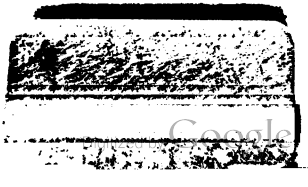
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CHEMISTRY

DESCRIPTIVE AND THEORETICAL

PART I.



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A

MANUAL OF CHEMISTRY

DESCRIPTIVE AND THEORETICAL

BY

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PART I.



LONDON

LONGMAN, GREEN, LONGMAN, AND ROBERTS

1861

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THIS Manual purposes, not only to satisfy a want felt, it is believed, by many teachers of Chemistry, but also to show how the employment of unitary formulæ facilitates the generalisation of chemical truths.

The views, of which it is an exponent, are based on those originally promulgated by Laurent and Gerhardt in France. They are now adopted by a large section of English chemists, particularly by Professors Williamson, Brodie, and Hofmann, whose researches have contributed greatly to their development.

The work was undertaken more especially at the request of Professor Brodie, who wished to have, for the use of his class at Oxford, a chemical text-book arranged in accordance with his own method of teaching.

It is characterised by the following features, in most of which it will be found to differ from other chemical manuals of similar scope :—

As a rule, the atomic weights selected for volatile elements represent single volumes, and those for volatile compounds double volumes, of their respective gases or vapours.

The great majority of compound bodies are expressed,

3229

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as unitary molecules, by unitary formulæ, instead of by additive, or, as they are commonly called, rational formulæ. Throughout, the algebraic sign of addition is never used to express combination.

The equivalent notation, by means of dashes, introduced by the author some years ago, and now constantly used in the original papers of most European chemists, is here employed for the purposes of elementary teaching.

The arrangement of the book is more than ordinarily systematic. The mutual relations of the elements and of their analogous compounds are largely dwelt upon, as are also the mutual relations of the various heterologous compounds of the same element. The properties of classes of bodies, chlorides, oxides, sulphates, &c., are described with greater fulness than is customary in text-books.

The compounds of mineral and organic chemistry are not considered apart in separate sections. Moreover, the doctrines of series, types, and substitutions, are applied indiscriminately to both branches of chemical science.

The technological applications of chemistry are but very briefly referred to, and the physics of chemistry only incidentally discussed; so that a more than usual proportion of space is devoted to chemistry proper, and especially to the description of chemical reactions.

In the compilation of this Manual, original memoirs have been largely consulted; while many statements scattered throughout its pages are based upon special experiments of the author's. Free use has likewise been made of the stores of information collected in Watts' Edition of Gmelin's *Handbook of Chemistry*, in Graham's *Elements of Chemistry*,

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and Watts' Supplement thereto; in Gerhardt's *Traité de Chimie Organique*, in Laurent's *Méthode de Chimie*, in Kekulé's *Lehrbuch der Organischen Chemie*, and in Miller's *Elements of Chemistry*.

The book will be completed in two or at the most in three parts, the second of which is expected to be ready by the ensuing summer.

The author has to express his best thanks to his friend Mr. Watts, for his kindness in revising the proof sheets, and for many valuable suggestions.

Guy's Hospital, October 1st, 1861.

*** The system of unitary formulæ, adopted by the author, is also employed in Mr. F. T. Conington's *Handbook of Chemical Analysis*, which was intended to serve, for laboratory use, as a companion work to this.

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CONTENTS.

CHAPTER I.

§ I. **General Considerations.** 1—32.

Paragraph		Page
1.	Chemical phenomena	1
2.	Elementary bodies	1
3.	Chlorous and basylous functions	1
4.	Groupings of the elements	2
5.	Proportional numbers	2
6.	Symbolic notation	4
7.	Chemical equations	4
8.	Combination by volume	4
9.	Comparable molecules	5
10.	Relation of gases to pressure and temperature	6
11.	Equivalent substitution	6
12.	Molecular types	8
13.	Homologous series	8
14.	Isologous series	9
15.	Heterologous series	10
16.	Acids	10
17.	Salts	11
18.	Acid-salts	11
19.	Basicity of acids	12
20.	Derived acids	13
21.	Anhydrides	14
22.	Aldehyds	14
23.	Amides	15
24.	Compound radicals	16
25.	Double decomposition	18
26.	Diamerones	18
27.	Crystallization	19
28.	Composite and hemihedral forms	23
29.	Isomorphism	24
30.	Polymorphism	26
31.	Allotropy	26
32.	Isomerism	27
33.	Atomic volume	28
34.	Atomic heat	29
35.	Diffusion and collection of gases	30

§ II. **Hydrogen.** 32—40.

36.	Distribution	32
37.	Preparation	32
38.	General properties	34
39.	Reducing action	35
40.	Relation to the hydrocarbons	35
41.	Halogen and metal substitutions	36
42.	Relation to the metals	37
43.	Metallic character?	39
44.	Relation to compound radicles	39
45.	Summary	39

CHAPTER II.

46.	The monhydric elements	41

§ I. **Chlorine.** 41—63.

47.	Distribution	41
48.	Preparation	41
49.	General properties	42
50.	Substitutions	43

CHLORHYDRIC ACID.

51.	History	44
52.	Preparation	44
53.	General properties	45
54.	Aqueous solution	46

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CHLORIDES.

Paragraph — Page

55. Classification 47
56. Preparation 50

CHLORINE AND OXYGEN.

57. Mutual relations of the oxides 51
58. Hypochlorous anhydride . 53
59. Hypochlorous acid. . . . 54
60. Hypochlorites 55
61. Chlorous anhydride . . 57
62. Chlorous acid 57
63. Chlorites 58
64. Chloric acid 58
65. Chlorates 58
66. Perchloric acid . . . 59
67. Perchlorates 60
68. Perchloric oxide . . . 61
69. Euchlorine 62

§ II. Bromine. 63—69.

70. Distribution 63
71. Preparation 63
72. Properties 64

BROMHYDRIC ACID.

73. Preparation 64
74. Properties 65

BROMIDES.

75. Classification. 66
76. Preparation 66

BROMINE AND OXYGEN.

77. Mutual relations of the oxides 67
78. Hypobromous acid and salts . 68
79. Bromic acid 68
80. Bromates 68

81. Chloride of bromine . . 69

§. III. Iodine. 69—77.

82. Distribution 69
83. Preparation 69
84. Properties 70

IODHYDRIC ACID.

85. Preparation 71
86. Properties 72

IODIDES.

87. Classification and properties . 72
88. Preparation 73

IODINE AND OXYGEN.

Paragraph — Page

89. Mutual relations 74
90. Iodic anhydride 74
91. Iodic acid 74
92. Iodates 75
93. Periodic anhydride . . 76
94. Periodic acid. 76
95. Periodates 76

96. Chlorides and bromides of iodine 77

§ IV. Fluorine. 77—81.

97. Distribution and properties . 77

FLUORHYDRIC ACID.

98. Preparation 78
99. Properties 79

FLUORIDES.

100. Preparation and properties . 80

§ V. The Halogen Group. 81—83.

101. Properties and mutual relations 81
102. Double halogen salts . . 82

CHAPTER III.

103. The dihydric elements . . 84

§ I. Oxygen. 84—139.

104. Distribution, &c. . . . 84
105. Preparation 84
106. General properties. . . 86
107. Oxidation at ordinary temperatures 87
108. Oxidation at a red heat . . 87
109. Combustion 88
110. Eremacausis—animal heat . 89
111. Oxygen substitutions . . 89
112. Acidification 89

OZONE.

113. History, &c. 90
114. Preparation 91
115. Constitution 93
116. General properties . . 94

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WATER.

Paragraph — Page

117. Distribution, &c. . . . 95
118. Composition 96
119. Combination of oxygen and hydrogen 99
120. General properties . . . 101
121. Freezing—ice . . . 102
122. Boiling—steam . . . 104
123. Decompositions . . . 109
124. Water of constitution . . 110
125. Solution of salts . . . 112
126. Absorption of gases . . 114
127. Natural waters . . . 118

PEROXIDE OF HYDROGEN.

128. Preparation 122
129. Properties 123

OXIDES AND HYDRATES.

130. Classification 127
a. Protoxides, &c. . . 128
β. Deutoxides, &c. . . 129
γ. Tritoxides, &c. . . 132
131. Distribution 134
132. Preparation 135
133. Properties 137

§ II. **Sulphur.** 139—186.

134. Distribution 139
135. Purification 140
136. Preparation 146
137. General properties . . 141
138. Allotropic forms . . . 142
139. Combinations . . . 145
140. Relations to oxygen, &c. . 146

SULPHYDRIC ACID.

141. Preparation 147
142. Properties 148
143. Reactions with metallic salts . 149

PERSULPHIDE OF HYDROGEN.

144. Preparation and properties . 150

SULPHIDES AND SULPHYDRATES.

145. Classification . . . 151
146. Preparation 155
147. Properties 156

SULPHUR AND CHLORINE.

148. Mutual relations of the chlorides 157
149. Protosulphide of chlorine . 158
150. Persulphide of chlorine . . 158
151. Tetrachloride of sulphur . 159

SULPHUR AND OXYGEN.

152. Mutual relations of the oxides 159
153. Sulphurous chloraldehyd . 161
154. Sulphuric chloraldehyd . . 161
155. Chlorhydrosulphurous acid . 163
156. Sulphurous anhydride, acid and salts 164
157. Sulphurous anhydride . . 164
158. Sulphurous acid . . . 166
159. Sulphites 167
160. Sulphuric anhydride, acid, and salts 167
161. Sulphuric anhydride . . 168
162. Sulphuric acid . . . 169
163. Its properties . . . 173
164. Sulphates: their varieties . 175
165. Their preparation . . . 180
166. Thiosulphuric acid . . 182
167. Thiosulphates or hyposulphites 182
168. Polythionic series . . . 184
169. Dithionic acid . . . 184
170. Trithionic acid . . . 185
171. Tetrathionic acid . . . 185
172. Pentathionic acid . . . 185

§ III. **Selenium.** 186—191.

173. Distribution 186
174. Preparation 186
175. Properties 187

SELENHYDRIC ACID.

176. Preparation and properties . 188

177. Selenides and selenhydrates . 188

178. Chlorides of selenium . . 189

SELENIUM AND OXYGEN.

179. Oxide of selenium . . 189
180. Selenious anhydride . . 189
181. Selenious acid . . . 189
182. Selenites 190
183. Selenic acid 190
184. Seleniates 191

185. Sulphides of selenium . . 191

Digitized by Google

§ IV. Tellurium. 192—197.

Paragraph Page
186. Distribution 192
187. Preparation 192
188. Properties 192

Tellurhydric Acid.

189. Preparation and properties . 193
190. Tellurides and tellurhydrates. 193
191. Chlorides of tellurium . . 193

Tellurium and Oxygen.

192. Tellurous anhydride . . 194
193. Tellurous acid . . . 194
194. Tellurites 194
195. Telluric anhydride . . 195
196. Telluric acid . . . 195
197. Tellurates 196

198. Sulphides of tellurium . . 196

§ V. The Oxygen Group. 197—203.

199. Mutual relations . . . 197
200. Relations to the halogens . 200
201. The water type . . . 201

CHAPTER IV.

202. The trihydric elements . . 204

§ I. Nitrogen. 204—275.

203. Distribution 204
204. Preparation 204
205. Properties 206

Atmospheric Air.

206. History, &c. 207
207. Ratio of oxygen to nitrogen . 208
208. Moisture and carbonic anhydride 209
209. Physical characters . . 212
210. Invariability of composition . 214

Ammonia.

211. History and distribution . 217
212. Formation 218
213. Preparation 219
214. Properties 219
215. Aqueous solution . . . 221
216. Derivatives 222

Paragraph Page
217. Trichloramide . . . 223
218. Diniodamide . . . 223

Ammoniacal Salts.

219. Constitution 224
220. Theory of ammonium . . 225
221. Decompositions . . . 226
222. Results of dehydration . . 227
223. Fluoride of ammonium . . 229
224. Chloride 229
225. Bromide 231
226. Iodide 231
227. Cyanide 231
228. Hydrate 231
229. Sulphydrate . . . 232
230. Sulphide 233
231. Bisulphide . . . 233
232. Selenhydrate . . . 234
233. Amides 234
234. Chlorate 235
235. Perchlorate . . . 236
236. Nitrite 236
237. Nitrate 236
238. Formate 237
239. Acetate 237
240. Cyanate 238
241. Sulphocyanate . . . 238
242. Acid sulphite . . . 238
243. Sulphite 239
244. Acid sulphate . . . 239
245. Sulphate 239
246. Acid carbonate . . . 240
247. Carbonate 240
248. Sesquicarbonate . . . 240
249. Sulpho-carbonate . . . 241
250. Acid oxalate . . . 242
251. Oxalate 242
252. Quadroxalate . . . 242
253. Acid stannate . . . 242
254. Phosphite 243
255. Bi-acid phosphate . . . 243
256. Monacid phosphate . . 243
257. Phosphate 243
258. Arsenites 243
259. Biacid arsenate . . . 244
260. Monacid arsenate . . . 244
261. Arsenate 244
262. Biacid cyanurate . . . 244
263. Biborate 245

264. Ammoniated salts . . . 245

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NITROGEN AND OXYGEN.

Paragraph — Page

265. Ortho- and meta-compounds 247
266. Mutual relations . . . 248
267. Nitrous oxide . . . 249
268. Its properties . . . 250
269. Nitric oxide 251
270. Its properties . . . 252
271. Chloride of azotyl . . . 254
272. Bichloride of azotyl . . 254
273. Aqua regia 255
274. Nitrous anhydride, acid, and salts 255
275. Nitrous anhydride . . . 256
276. Nitrous acid 257
277. Nitrites 257
278. Pernitric oxide . . . 259
279. Its properties . . . 259
280. Chloride of nitryl . . . 261
281. Nitric anhydride . . . 262
282. Nitric acid 263
283. Its properties . . . 264
284. Nitrates 267
285. Their properties . . . 268

NITROGEN AND SULPHUR.

286. Classification of compounds . 269
287. Thionamide 269
288. Thionamic acid . . . 270
289. Sulphamide 270
290. Sulphamic acid . . . 271
291. Bisulphide of nitrogen . . 272
292. Nitro-sulphates . . . 272
293. Sulphazotized salts . . 273
294. Sulphates of azotyl . . 274

§ II. **Phosphorus.** 275—318.

295. Distribution, &c. . . . 275
296. Manufacture 276
297. Properties 277
298. Allotropic forms . . . 279

PHOSPHORETTED HYDROGEN.

299. History and preparation . 280
300. Properties 282
301. Relations to ammonia . . 283
302. Liquid phosphide of hydrogen 284
303. Solid phosphide of hydrogen . 285
304. Phosphides 285

PHOSPHORUS AND THE HALOGENS.

305. Trichloride 286
306. Pentachloride . . . 286
307. Oxichloride 287
308. Sulphochloride . . . 287
309. Bromides 288
310. Iodides 288

PHOSPHORUS AND OXYGEN.

311. Mutual relations . . . 289
312. Suboxide of phosphorus . 291
313. Hypophosphorous acid . . 292
314. Hypophosphites . . . 292
315. Phosphorous anhydride . . 293
316. Phosphorous acid . . . 294
317. Phosphites 295
318. Phosphoric acid . . . 295
319. Meta-compounds . . . 296
320. Pyro-compounds . . . 299
321. Complex compounds . . 301
322. Phosphoric anhydride . . 302
323. Metaphosphoric acid . . 302
324. Metaphosphates . . . 303
325. Their varieties . . . 304
326. Pyrophosphoric acid . . 305
327. Pyrophosphates . . . 305
328. Orthophosphoric acid . . 306
329. Its properties . . . 308
330. Orthophosphates . . . 309
331. Their preparation . . . 311
332. Sulphides of phosphorus . 313

PHOSPHORUS AND NITROGEN.

333. Mutual relations . . . 314
334. Phosphorosamide . . . 314
335. Chloronitride of phosphorus . 315
336. Monophosphamide . . 315
337. Phosphamic acid . . . 316
338. Phosphodiamide . . . 317
339. Phosphotriamide . . . 317

§ III. **Arsenic.** 318—345.

340. Distribution, &c. . . . 318
341. Manufacture 319
342. Properties 319
343. Reduction test . . . 320

ARSENETTED HYDROGEN.

344. Preparation 321
345. Properties 321
346. Derivatives 322
347. Marsh's test . . . 323
348. Solid hydride of arsenic . 326
349. Arsenides 326

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ARSENIC AND THE HALOGENS.

Paragraph — Page

350. Trifluoride 327
351. Trichloride 327
352. Tribromide 329
353. Teriodide 329

ARSENIC AND OXYGEN.

354. Mutual relations . . . 329
355. Arsenious anhydride . . 330
356. Its allotropic forms . . 331
357. Its properties . . . 332
358. Arsenious acid . . . 333
359. Reinsch's test . . . 334
360. Arsenites 335
361. Arsenic anhydride . . 336
362. Arsenic acid 336
363. Meta- and para-compounds . 338
364. Arsenates 338

ARSENIC AND SULPHUR.

365. Disulphide 340
366. Trisulphide 341
367. Sulpharsenites . . . 343
368. Pentasulphide . . . 344
369. Sulpharsenates . . . 344

§ **IV. Antimony.** 345—363.

370. Production 345
371. Properties 346

ANTIMONETTED HYDROGEN.

372. Preparation 348
373. Properties 349
374. Antimonides . . . 350

ANTIMONY AND THE HALOGENS.

375. Trichloride 351
376. Pentachloride . . . 351
377. Tribromide, &c. . . . 352

ANTIMONY AND OXYGEN.

378. Teroxide 352
379. Antimonious hydrate . . 353
380. Its reactions 353
381. Tetroxide 355
382. Pentoxide 356

Paragraph — Page

383. Antimonic acid . . . 356
384. Antimonates . . . 357

ANTIMONY AND SULPHUR.

385. Oxisulphide 358
386. Trisulphide 359
387. Sulphantimonites . . . 360
388. Pentasulphide . . . 362
389. Sulphantimonates . . . 362

390. Salts of antimony . . 363

§ **V. Bismuth.** 363—371.

391. Distribution and production . 363
392. Properties 364

BISMUTH AND THE HALOGENS.

393. Trichloride 365
394. Tribromide 365

BISMUTH AND OXYGEN.

395. Teroxide 366
396. Hydrate 366
397. Bismuthous salts . . . 367
398. Pentoxide 367
399. Bismuthic acid . . . 368
400. Tetroxide and suboxide . 368

BISMUTH AND SULPHUR.

401. Disulphide 368
402. Trisulphide 369
403. Sulphotelluride . . . 369

SALTS OF BISMUTH.

404. Nitrate 370
405. Sulphate 370
406. Carbonate 371
407. Oxalate 371
408. Phosphate 371

§ **VI. The Nitrogen Group.** 371—380.

409. Mutual relations . . . 371
410. Relations to the halogen and oxygen families . . . 375
411. The ammonia-type . . 376
412. Mixed types . . . 379

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ERRATA.

Page	*Line*	*Error*	*Correction*
10	5	$C_5H_4, C_{10}H_8$,	$C_5H_8, C_{10}H_{16}$,
37	20	PtC_2	$PtCl_2$
43	9	C_8H_{20}	$C_{10}H_{16}$
46	3	480	458
49	3 from bottom	two	three
57	3	$2MnHO_2$	$Mn_2O_2.H_2O$
73	5 from bottom	replacement metal	replacement of metal
76	5	I_5O_2	I_2O_5
156	5	C_2	C_4
176	1 and 9	hexahydrated	terhydrated
176	bottom	six	three
275	12 from bottom	15·5	62
291	14	HP_3O_3	H_3PO_3
301	4	$+H_2O$	*delete*.
314	20	PH'''_3O_3	$P'''H_3O_3$

In the table, on page 176, the double sulphates represented with 6, should be represented with 3 atoms of crystallisation-water.

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MANUAL OF CHEMISTRY.

CHAPTER I.

§ I. General Considerations.

(1) Chemical phenomena.—Chemistry treats of the composition of bodies. Generally speaking, all changes in the state of bodies that are not attended by an alteration of composition belong to the province of physics; while all changes that are attended by an alteration of composition belong to the province of chemistry. But the two classes of phenomena are so intimately associated with each other, that it is impossible to draw any absolute line of demarcation between them.

(2) Elementary bodies.—Chemists are acquainted with about sixty different kinds of matter, which have hitherto proved undecomposable, and are consequently termed simple bodies, or elements. These elements unite with one another in certain fixed or definite proportions, to form an infinite variety of compound bodies. Among the elements are included substances having the most diverse characters. The great majority exist in the solid state; bromine and mercury are liquid; while oxygen, hydrogen, nitrogen, and chlorine, are gaseous. About four fifths of the elements are metallic, as instanced by gold, silver, copper, iron, &c.; the remainder are non-metallic, as instanced by carbon, sulphur, phosphorus, &c.

(3) Chlorous and basylous functions.—It is found, as a general rule, that elements which have the strongest tendencies to combine with one another, are possessed of opposite properties. The metals potassium and sodium, and their congeners, which constitute the basylous class of elements, are characterised in the highest degree by one set of properties; while chlorine, and the bodies more or less allied to it, which constitute the chlorous or acidulous class, are characterised by an opposite set.

Under certain conditions, very many chemical compounds are

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decomposed when traversed by the electric current. As a result of this electrolytic decomposition, the basylous elements are liberated at the negative pole, and are thence termed electro-positive, as an inference from the well-known law, that oppositely electrified bodies attract one another; while the chlorous elements are liberated at the positive pole, and are thence termed electro-negative. But chlorous or electro-negative, and basylous or electro-positive, elements are not separated from one another by any peculiar distinctive character; they are but as links, at either end of a long chain, and approximate to one another by insensible gradations. An element is negative to those on one side of it, positive to those on the other. Thus even sulphur, which is essentially chlorous in its habitudes, is nevertheless positive in respect to oxygen, and is liberated from its oxide at the negative pole.

(4) GROUPINGS OF THE ELEMENTS.—The elements are capable of being distributed into certain natural groups, or families. They are associated with one another into these groups, chiefly by the similar constitution of their combinations, partly by the similar character of their combinations, and partly by the correlations of their proportional numbers and atomic volumes, to which we shall again refer. Some groups are remarkable for the equal properties, others for the gradational properties, of their members. Thus we have a group comprising phosphorus, which is electro-negative, arsenic, which is intermediate, and antimony, which is electro-positive. These three elements are most intimately related to one another, but their properties are sequential. On the other hand, calcium, strontium, and barium, which correspond very closely in their characters, are all basylous, and that to very much the same extent. Two or three classes of elements are referred to by special names. Thus, fluorine, chlorine, bromine, and iodine, are known as the halogens. Lithium, sodium, and potassium, are known as the alkali-metals, and their salts as alkaline salts. Calcium, strontium, and barium, constitute the alkaline-earth metals; while magnesium and aluminum, though belonging to different natural groups, are, together with several rarer metals, distinguished as the earth-metals proper.

(5) PROPORTIONAL NUMBERS.—To every element there is assigned a particular number, termed its proportional number, which expresses the least indivisible proportion of the element that is found to enter into a combination; and as the relative quantity of hydrogen that can enter into a combination proves to be less than that of any other element, its combining proportion is taken as the standard of comparison, or unity. The doctrine of combination in

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definite and multiple proportions teaches us that the elements combine with one another, only in the ratios indicated by their proportional numbers, or by multiples of those numbers. Thus we have two combinations of chlorine and mercury, namely, corrosive sublimate and calomel. In the former, the ratio of the chlorine to the mercury is as 35·5 to 100, in the latter, as 35·5 to *twice* 100; the proportional numbers of chlorine and mercury being 35·5 and 100 respectively. The determination of what is the smallest indivisible combining proportion, or *chemical atom*, of a body involves the consideration of very many circumstances that we shall hereafter have to discuss somewhat minutely. The following table exhibits a list of the elements, with their proportional numbers or atomic weights, and their symbols or abbreviated names.

SYMBOLS AND PROPORTIONAL NUMBERS OF THE ELEMENTS.

H	Hydrogen	1		Mg	Magnesium	12
				Zn	Zinc	32·5
F	Fluorine	19		Cd	Cadmium	56
Cl	Chlorine	35·5				
Br	Bromine	80		Hg	Mercury (*Hydrargyrum*)	100
I	Iodine	127		Pb	Lead (*Plumbum*)	103·5
				Ag	Silver (*Argentum*)	108
O	Oxygen	16				
S	Sulphur	32		Cr	Chromium	26
Se	Selenium	80		Mn	Manganese	27
T	Tellurium	128		Fe	Iron (*Ferrum*)	28
				Ni	Nickel	29
N	Nitrogen	14		Co	Cobalt	30
P	Phosphorus	31		Cu	Copper (*Cuprum*)	31·7
As	Arsenic	75				
Sb	Antimony (*Stibium*)	120		Al	Aluminum	13·7
Bi	Bismuth	208		Zr	Zirconium	33·5
				Ce	Cerium	46
C	Carbon	12		La	Lanthanum	47
Si	Silicon	28·5		D	Didymium	48
Ti	Titanium	48·5		U	Uranium	60
Sn	Tin (*Stannum*)	118				
Ta	Tantalum	138		Mo	Molybdenum	48
				Vd	Vanadium	68·5
B	Boron	11		W	Tungsten (*Wolfram*)	92
Li	Lithium	7		Au	Gold (*Aurum*)	197
Na	Sodium (*Natrium*)	23				
K	Potassium (*Kalium*)	39		Ro	Rhodium	52
				Ru	Ruthenium	52
Ca	Calcium	20		Pd	Palladium	53
Sr	Strontium	44				
Ba	Barium	68·5		Pt	Platinum	98·5
				Ir	Iridium	98·5
G	Glucinum	4·7		Os	Osmium	99·5
Y	Yttrium	32				
Th	Thorium	59·5				

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(6) SYMBOLIC NOTATION.—Each symbol represents one combining proportion, or atom, of the element. Thus N means 14 parts by weight of nitrogen as compared with 1 part by weight of hydrogen. Combination is represented by the apposition of symbols; thus KCl, or chloride of potassium, signifies 39 parts of potassium united with 35·5 parts of chlorine. A small figure placed to the right of a symbol indicates a multiple quantity of that particular element. Thus C_2H_6O, or alcohol, signifies a compound of two proportions of carbon, six of hydrogen, and one of oxygen. A larger figure placed to the left of an allocation of symbols, multiplies the entire compound. Thus, $3H_2SO_4$ represents three proportions of sulphuric acid, a compound body, consisting of two atoms of hydrogen, one of sulphur, and four of oxygen. The single formula of a compound body represents the smallest indivisible proportion, or the atom, or molecule, of that particular compound; and its proportional number, or atomic weight, is the sum of the atomic weights of its constituents. Thus the atomic weight of benzoic acid, $C_7H_6O_2$, $=(12\times7)+(1\times6)+(16\times2)=122$. In bodies of a complex constitution, and particularly when comparing somewhat complex bodies with others of a more simple character, it is sometimes found advisable to break up the formulæ by means of periods, brackets, parentheses, &c. Thus for aniline, we sometimes write $C_6H_5.H_2N$, instead of C_6H_7N; for nitrate of ammonium, $\overset{\frown}{NH_4}NO_3$ instead of $N_2H_4O_3$; for common alum, $KAl_2(SO_4)_2.12H_2O$ instead of $KAl_2S_2O_8.12H_2O$, or $KAl_2S_2O_{20}H_{24}$. Sometimes these breaks are purely arbitrary or conventional, at other times they indicate a real molecular isolation of one portion of a compound from the remainder. Thus the twelve atoms of water that enter into the composition of crystallized alum, seem to have an independent existence within the salt, quite separate from the other constituents.

(7) CHEMICAL EQUATIONS.—The signs +, —, and =, are used almost in their ordinary algebraical sense. The sign + signifies addition to, or rather mixture with; the sign — abstraction from; and the sign = equivalency with, or rather conversion into. Thus the equation $2HCl+Cu_2O=2CuCl+H_2O$, implies that two atoms of chlorhydric acid, mixed with one atom of oxide of copper, yield two atoms of chloride of copper, and one atom of water. Or the reaction may, of course, be written, $2HCl+Cu_2O-H_2O=2CuCl$.

(8) COMBINATION BY VOLUME.—Hydrogen being the lightest substance in nature is conveniently taken as a standard for the specific gravities of gases. It is found that the particular bulk, or

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volume, which corresponds to any given quantity, say 1 gramme, of hydrogen, corresponds to 14 grammes of nitrogen, to 16 grammes of oxygen, to 35·5 grammes of chlorine, to 80 grammes of bromine, &c.; and, in general, that the specific gravities, or comparative weights of equal volumes, of the elementary gases and vapours, coincide with their atomic weights, so that the symbols H, N, O, Cl, Br, &c., represent equal volumes of the respective elements. Hence the formula HCl, chlorhydric acid, implies a combination of one volume of hydrogen with one of chlorine, ; H_2O, or water, implies a combination of two volumes of hydrogen with one of oxygen, ; H_3N, or ammonia, implies a combination of three volumes of hydrogen with one of nitrogen, ; &c.

(9) COMPARABLE MOLECULES.—The specific gravities of elementary bodies when in the gaseous state being identical with their atomic weights, the specific gravities of compound bodies, under the same circumstances, are found to coincide with the halves of their atomic weights. We know that specific gravity is defined to be "the weight of a unit of volume," and hence the atomic weight of a compound body, being the double of its specific gravity, must represent the weight of two units of volume. In other words, the molecules of all compound bodies, when in the gaseous state, occupy the same volume, which is exactly double the volume of an atom or proportion of hydrogen; so that if we represent an atom of hydrogen or other gaseous element by , we must represent the atom of a gaseous compound by . No matter what the number of atoms or volumes, that enter into the constitution of any volatile compound, they all become condensed into two volumes, as shown by the fact that the specific gravity, or vapour density, of the compound is the half of its atomic weight. There are, however, some exceptions to this general law, which will have to be separately considered.

Seeing that the molecule of a compound body corresponds with two volumes of gas or vapour, and the atom of an element with but one volume, it is evident that the quantity of an element which is strictly comparable to the molecule of a compound body, must be represented by two atoms. Hence the symbols, , , , or HH, HCl, ClCl, represent comparable quantities of the three bodies, hydrogen, chlorhydric acid, and chlorine respectively, which, thus formulated, present an obvious relation of sequence to

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one another. By the molecule of an element, therefore, we invariably understand two atoms, or two volumes; and there is great reason to believe that our acquaintance with the uncombined elements pertains exclusively to their molecules. So that while Cl for instance represents the atom, or smallest proportion of chlorine that can enter into a combination, Cl_2 represents the molecule, or smallest proportion of free chlorine that can result from, or effect, a reaction. There are certain compound molecular groupings, which, like the elementary molecules, occupy two volumes when in the free state, and become halved in combination. Thus ethyl in the free state is represented by $C_4H_{10} = \square\square$, in the combined state by $C_2H_5 = \square$.

(10) RELATION OF GASES TO PRESSURE AND TEMPERATURE.—The volume of a given quantity of any gas is affected by the pressure and temperature to which it is exposed according to two general laws, which must be had regard to in any comparison of the volumes of different gases. The law of Boyle and Marriotte affirms that the volume of a gas is inversely as the pressure to which it is subjected; this pressure being usually measured in inches or millimetres of mercury. The law of Dalton and Gay Lussac affirms that the volume of a gas is increased, or decreased, by $\frac{1}{273}$ of its bulk at zero, for every centigrade degree of temperature above, or below, zero.* These two laws apply equally to vapours, when at temperatures considerably above their condensing points. Hence two volumes of gas or vapour, at very different pressures and temperatures, may be compared with one another, provided the proper corrections are applied according to the following formulæ:— 1°. As x inches or millimetres are to y inches or millimetres, so is bulk at y to bulk at x. 2°. As $273 \pm x$ is to $273 \pm y$ so is bulk at x degrees above or below zero, to bulk at y degrees. Regnault has shown that neither of these laws is absolutely accurate, especially in reference to the condensable gases, but the variations are for the most part exceedingly minute, and, except in special experiments, may be altogether disregarded.

(11) EQUIVALENT SUBSTITUTION.—Not only do we adopt hydrogen as our standard of atomic weight, and of specific gravity, but we also make it our standard of equivalency, or interchangeable value. It is found that the hydrogen of different compounds may be replaced by elements of the most diverse characters; by the electro-positive metals on the one hand, and by electro-negative chlorine and its congeners on the other. Even similarly functioned

* Or $\frac{1}{491}$ of its bulk at Fahrenheit's zero, for every Fahrenheit degree.

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elements, however, differ among themselves in reference to the quantities of hydrogen which they can replace, or for which they can be substituted. The atoms of different metals, for instance, can replace respectively one half, one, one and a half, two, three, four, and five, atoms of hydrogen; and occasionally an atom of the same metal, under different conditions, can replace two different quantities of hydrogen. We find that one atom of potassium invariably replaces one atom of hydrogen, and that substitution in this case can only be effected by the interchange of an equal number of atoms; but in the substitution of bismuth for hydrogen, the one single atom of bismuth is invariably exchanged for three atoms of hydrogen. So that, starting from phosphoric acid H_3PO_4, for example, we can procure by substitution, K_3PO_4 phosphate of potassium, and $BiPO_4$ phosphate of bismuth. The equivalent, or replaceable value, of the atom of bismuth, therefore, is three times as great as that of hydrogen; and we sometimes mark its symbol with three dashes to indicate that fact, thus: Bi‴. The mult-equivalent character of other metals may also be illustrated by means of the phosphates, as shown below: —

	H_3PO_4	Phosphoric acid.
	Ag'_3PO_4	Phosphate of silver.
Na'_3PO_4, $Na'H_2PO_4$	and Na'_2HPO_4	Phosphates of sodium.
	$Sn''HPO_4$	Phosphate of tin.
	$Sb'''PO_4$	Phosphate of antimony.
Fe'_3PO_4	and $(Fe_2)'''PO_4$	Phosphates of iron.
Hg'_3PO_4	and „ Hg_6PO_4	Phosphates of mercury.

The atom of mercury is equivalent, sometimes to one, sometimes to half an atom of hydrogen. The atom of iron is equivalent sometimes to one, sometimes to one and a half atoms of hydrogen. The atom of platinum is equivalent sometimes to one, sometimes to two atoms of hydrogen. This idea of equivalency is derived from a consideration of the phenomena of substitution. It is independent of any correspondence in the number of atoms compared, but relates solely to their special functions and relations; so that when an element has several functions, it has likewise several equivalents. Equivalency between any two bodies implies the capability of their being exchanged for one another. Thus there is no equivalency between an atom of potassium K, and an atom of acid sulphate of potassium $KHSO_4$. On the other hand, K'_3 represents three atoms of potassium, and Bi‴ one atom of bismuth, but the two quantities correspond to the same equivalent, or representative value, and the two quantities are mutually interchangeable, thus: $Bi'''(NO_3)_3 + 3K'I = 3K'NO_3 + Bi'''I_3$.

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(12) MOLECULAR TYPES. — Chemists are accustomed to say that bodies having analogy of constitution, and yielding analogous reactions, belong to the same type. The compounds of hydrogen with the other gaseous elements, and with carbon, namely, chlorhydric acid HCl, water H_2O, ammonia H_3N, and marsh gas H_4C, constitute types of the highest degree of generality, to which, especially, by the aid of certain simple conventions, very numerous and varied bodies are referrible. These general types are known respectively as the types chloride or hydride, oxide or hydrate, amide or nitride, and carbide. We also avail ourselves of multiple types, obtained by doubling or trebling the formulæ of the above primary molecules. Thus we say that diplatosamine N_2H_5Pt, belongs to the di-amide type, N_2H_6, or $2NH_3$. In addition to these general types we employ an indefinite number of special types. Thus we refer the two following series of compounds to the cyanate and ethylene types respectively.

CHNO	Cyanic acid.	C_2H_4	Ethylene.
CKNO	Cyanate of potassium.	C_2H_3Cl	Chlor-ethylene.
CHNS	Sulphocyanic acid.	$C_2H_2Cl_2$	Bichlor-ethylene.
CPbNS	Sulphocyanate of lead.	$C_2H\,Cl_3$	Trichlor-ethylene.
CHNSe	Selenocyanic acid.	$C_2\quad Cl_4$	Tetrachlor-ethylene.

The association of bodies by means of a common type is not confined to compounds containing an equal number of elementary atoms, but pertains to bodies with very unequal numbers of atoms, provided they correspond to the same equivalent value; as illustrated by diplatinamine N_2H_4Pt'', which belongs to the di-amide type, N_2H_6, by hydrate of gold $Au'''H_3O_3$, which belongs to the ter-hydrate type, H_6O_3, and by the various compounds shown in a preceding table, which all belong to the phosphate type.

These different molecular types are persistent throughout that normal double decomposition which constitutes the most frequent case of chemical action. Two bodies belonging to the same, or more frequently, to different types, react upon one another with mutual interchange of certain of their constituents, to form two new bodies belonging to the original types. Thus, $\left.\begin{matrix}K\\H\\H\end{matrix}\right\}N$ potassamide, and $\left.\begin{matrix}H\\H\end{matrix}\right\}O$ water, yield $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$ ammonia, and $\left.\begin{matrix}K\\H\end{matrix}\right\}O$ hydrate of potassium.

(13) HOMOLOGOUS SERIES. — Throughout the whole range of chemistry, the compounds of carbon are preeminent for their number and variety. Gerhardt first brought prominently into notice the circumstance that carbon compounds might be arranged

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in what he termed homologous series, the successive terms of each of which differed from one another in composition by an increment of CH_2, as illustrated in the following table.

Hydrocarbons.		Monobasic Acids.		Alkaloids.	
C_6H_6	Benzene.	CH_2O_2	Formic.	CH_5N	Methylia.
C_7H_8	Toluene.	$C_2H_4O_2$	Acetic.	C_2H_7N	Ethylia.
C_8H_{10}	Xylene.	$C_3H_6O_2$	Propionic.	C_3H_9N	Propylia.
C_9H_{12}	Cumene.	$C_4H_8O_2$	Butyric.	$C_4H_{11}N$	Butylia.
$C_{10}H_{14}$	Cymene.	$C_5H_{10}O_2$	Valeric.	$C_5H_{13}N$	Amylia.
&c.	&c.	&c.	&c.	&c.	&c.

The members of any homologous series are remarkable for the great resemblance in properties which they bear to their congeners near them in the scale, and for the gradual development of differences between them and their remote congeners. Thus, while there is considerable difference between the formic and valeric acids, there is very little between the formic and acetic, the acetic and propionic, the propionic and butyric, the butyric and valeric acids respectively. The general chemical habitudes of homologous bodies correspond, and their differences in properties like their differences in composition are gradational. Among other sequential variations, it is found that the boiling points of successive members of a homologous series increase regularly by 19° centigrade.

(14) Isologous series.—Carbon compounds may be arranged not only in homologous, but also in isologous series, the successive terms of each of which differ from one another by an increment of H_2. In the accompanying table of homologous and isologous hydrocarbons, the homologous series are arranged in perpendicular, the isologous in horizontal lines.

C_1H_2						
C_2H_4	C_2H_2					
C_3H_6	C_3H_4	C_3H_2				
C_4H_8	C_4H_6	C_4H_4	C_4H_2			
C_5H_{10}	C_5H_8	C_5H_6	C_5H_4	C_5H_2		
C_6H_{12}	C_6H_{10}	C_6H_8	C_6H_6	C_6H_4	C_6H_2	
C_7H_{14}	C_7H_{12}	C_7H_{10}	C_7H_8	C_7H_6	C_7H_4	C_7H_2
C_8H_{16}	C_8H_{14}	C_8H_{12}	C_8H_{10}	C_8H_8	C_8H_6	C_8H_4 &c.
C_9H_{18}	C_9H_{16}	C_9H_{14}	C_9H_{12}	C_9H_{10}	C_9H_8	C_9H_6 &c.
$C_{10}H_{20}$	$C_{10}H_{18}$	$C_{10}H_{16}$	$C_{10}H_{14}$	$C_{10}H_{12}$	$C_{10}H_{10}$	$C_{10}H_8$ &c.
&c.	&c.	&c.	&c.	&c.	&c.	&c.

Of the above compounds, the majority only are at present known to chemists. The isologous relations of bodies have been hitherto but little studied. We are, however, acquainted with several indirect means for transferring isologous compounds from one series of homologues into another; as when, for instance, propylic

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alcohol C_3H_8O, is converted into allylic alcohol C_3H_6O. Analogous compounds, which are neither homologous nor isologous, but in which the same ratio of carbon to hydrogen prevails, seem also to manifest a likeness to one another, as instanced by the terebinthinate hydrocarbons, C_5H_4, $C_{10}H_8$, &c.

(15) HETEROLOGOUS SERIES.—Members of homologous and isologous series respectively, manifest analogy of constitution and properties, and, as we shall hereafter see, may be referred to the same types; but the members of heterologous series are associated with one another chiefly by generation and mutual metamorphosis. With every hydrocarbon, for instance, there are associated numerous heterologous compounds, aldehyds, ethers, mercaptans, &c., differing greatly from one another, but each having its own series of homologues. The primary seriated heterologues are those which differ from one another by the number of their oxygen atoms, thus:—

Methylene . . . CH_2	C_2H_4 . . Ethylene.
Formic aldehyd* . CH_2O	C_2H_4O . . Aldehyd.
Formic acid . . . CH_2O_2	$C_2H_4O_2$. . Acetic acid.
Carbonic acid . . CH_2O_3	$C_2H_4O_3$. . Glycolic acid.
	$C_2H_4O_4$. . Glyoxylic acid?

We may of course associate with each hydrocarbon an infinite number of other heterologues which also have their respective homologues, but which do not admit of numerical seriation in relation to one another, and consequently do not form members of a heterologous series. Unlike the relations of homology and isology, the relation of seriated heterology is not confined to carbon compounds, but prevails in those of many other elements, as illustrated in the following table.

HCl Chlorhydric acid.	H_3P Phosphamine.	$H_2S\ O_6$ (wanting).
HClO Hypochlorous acid.	H_3PO Phosphoric aldehyd.*	$H_2S_2O_6$ Dithionic acid.
$HClO_2$ Chlorous acid.	H_3PO_2 Hypophosphorous acid.	$H_2S_3O_6$ Trithionic acid.
$HClO_3$ Chloric acid.	H_3PO_3 Phosphorous acid.	$H_2S_4O_6$ Tetrathionic acid.
$HClO_4$ Perchloric acid.	H_3PO_4 Phosphoric acid.	$H_2S_5O_6$ Pentathionic acid.

(16) ACIDS.—The essential character of an acid is its capability of exchanging hydrogen for a metal; but as in nearly all hydrogenised bodies, a part at least of the hydrogen may be directly or indirectly replaced by metal, it follows that all these bodies must analogically be considered as acids. From habit, however, we adopt one particular mode of replacement as our conventional

* These two aldehyds are known only in the form of their chloro-representatives, $C\,Cl_2O$ and $Cl_3P\,O$ respectively.

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criterion of acidity, namely, that effected by the hydrates of potassium and sodium. An acid is a hydrogenised body which, when treated with hydrate of potassium, can exchange hydrogen for potassium, with simultaneous formation of water, thus:—

$$H_3PO_4 + KHO = KH_2PO_4 + H_2O.$$

The solutions of these bodies are generally found to have the property of reddening blue litmus paper, and of effervescing with alkaline carbonates, but the possession of these properties is not necessarily essential to, or characteristic of an acid. It will be found that our definition excludes the binary compounds of hydrogen with oxygen, carbon, nitrogen, phosphorus, arsenic, and antimony respectively, from the conventional class of acids.

We may take as our general type for an acid the formula $H_xR_yO_z$, where H_x represents the atoms of hydrogen, which, save in carbon compounds, are found to vary only from 1 to 4; where R_y represents the acid radicle, that is the chlorine, or sulphur, or phosphorus, or carbon, &c., which gives the special character to the acid, and which, save in carbon compounds, is usually confined to 1 or 2 elementary atoms; and where O_z represents the atoms of oxygen which generally range from 0 to 4, but occasionally extend to higher numbers. Oxygenised acids are also called ternary, while non-oxygenised acids, or those in which $z=0$, are called binary. These binary acids were formerly known as hydracids.

(17) SALTS.—Precisely as all hydrogen compounds are analogically acids, so are all metallic compounds analogically salts, but conventionally we recognise as salts all metallic compounds that are obtainable, or that may be conceived as obtainable, from acids by the substitution of metal for hydrogen. Thus from chlorhydric acid HCl, we may produce chloride of potassium KCl. This mode of viewing a salt is the converse of Gerhardt's well-known definition of an acid, namely, "a salt whose base is hydrogen." Many salts, however, known as salts of the alkaloids, are formed by the direct union of their acids with certain nitrogenised or phosphorised compounds. Ammonia, for example, combines directly with chlorhydric acid to form chlorhydrate of ammonia, NH_3HCl. But salts of this character may also be represented to contain composite metals in place of the hydrogen of the acid. Thus NH_3HCl may be written NH_4Cl, chloride of ammonium, NH_4, a pseudo-metallic grouping, which in its combinations presents the most marked analogies to potassium: and so in other instances.

(18) ACID-SALTS.—Acids with only one atom of hydrogen are necessarily monobasic, or can only acquire one equivalent of metallic base in exchange for hydrogen. Acids with two atoms of

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hydrogen are generally bibasic, and can acquire either one or two equivalents of metal in exchange for hydrogen to form either acid or normal salts. Thus H_2SO_4 sulphuric acid, forms $KHSO_4$ acid-sulphate, and K_2SO_4 normal sulphate of potassium. In the same manner, acids with three and four atoms of hydrogen respectively, are usually tri- and tetrabasic, and form each, in addition to their normal salts, two and three varieties of acid salts. Thus arsenic acid H_3AsO_4, forms normal arsenate of sodium Na_3AsO_4, and two descriptions of acid arsenate, Na_2HAsO_4 and NaH_2AsO_4 respectively. Acid-salts constitute to all intents and purposes a variety of the class of acids, and for the most part react with vegetable colours and alkaline hydrates and carbonates, as do the normal acids, although indeed there are many exceptions.

(19) Basicity of acids. — But in acids with more than one, and especially with more than two atoms of hydrogen, the number of hydrogen atoms does not necessarily determine the basicity, because it does not follow that all the hydrogen atoms are replaceable by metal. Thus formic acid H_2CO_2 is not bibasic, neither is hypophosphorous acid H_3PO_2 tribasic, nor acetic acid $H_4C_2O_2$ tetrabasic. Moreover, by means of the metals alone we are frequently unable to determine with precision the basicity of an acid, for it happens occasionally that when we cannot replace a second or third atom of hydrogen by some particular metal, such as potassium, we can, especially by some indirect process, replace it by some other metal, such as lead. Now among the many clearly established points of difference between well-defined mono-, bi-, tri-, and tetrabasic acids, we find that their action upon the alcohols to form neutral ethers with as many as one, two, three, and four atoms of alcohol-residue respectively, is highly characteristic, and we accept this formation of ethers as a surer, though not as an absolute, criterion of the basicity of an acid; for indeed in the polyhydrogenised acids, the degree of basicity appears to be rather a habitual than a fixed attribute. Sometimes we can form higher ethers than salts, at other times by indirect means, higher salts than ethers.

In polyhydrogenised acids we generally find that the basicity, or quantity of hydrogen replaceable by metal, is determined by the degree of oxydation, as instanced particularly by the acids of phosphorus: —

		KH_2PO_2	H_3PO_2	Hypophosphorous	acids
	K_2HPO_3	KH_2PO_3	H_3PO_3	Phosphorous	and
K_3PO_4	K_2HPO_4	KH_2PO_4	H_3PO_4	Phosphoric	salts.

Thus hypophosphorous acid is monobasic, phosphorous acid bi-

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basic, and phosphoric acid tribasic, *quoad* their ordinary salts. With regard to carbon acids, it is generally found that those with two atoms of oxygen are decidedly monobasic, those with four atoms of oxygen decidedly bibasic, and those with three atoms of oxygen intermediate, forming indeed two classes of ethers, acid and neutral, with one and two atoms of alcohol-residue respectively; but, save by indirect means, forming only one class of salts, namely, those with one atom of metal.

(20) DERIVED ACIDS. — In oxygenised, or ternary, acids and salts, it is found that some or all of the oxygen atoms may be represented by sulphur, and probably also by its congeners, selenium and tellurium. Thus we have Na_2CO_3 carbonate or oxycarbonate, and Na_2CS_3 sulphocarbonate of sodium; K_3PO_4 phosphate or oxyphosphate, and K_3PO_3S sulphoxyphosphate of potassium. Bodies of this description are known as sulphur salts and sulphur acids respectively. These sulphur salts and acids are rarely, if ever, obtained by the direct substitution of sulphur for oxygen in the ready formed compounds.

In the polyhydrogenised acids, it is found that the hydrogen atoms which are not readily replaceable by basylous metals, are readily replaceable by a direct substitution of chlorine, bromine, or iodine. In this way we have produced,

$KH_3C_2O_2$	Acetate of potassium,
$H_4C_2O_2$	Acetic acid,
$H_3ClC_2O_2$	Chlor-acetic acid,
$H_2Br_2C_2O_2$	Bibrom-acetic acid,
$HCl_3C_2O_2$	Trichlor-acetic acid,
$KCl_3C_2O_2$	Trichlor-acetate of potassium.

Chloro-, &c., acids and salts usually possess properties very closely corresponding to those of their normal congeners. Some acids, in which the acid character is not strongly marked, may even be represented by chloro- compounds not containing any hydrogen whatever. Thus, we have KClO hypochlorite of potassium, HClO hypochlorous acid, and Cl_2O hypochlorous oxide or anhydride. But these cases are exceptional, and the chloro- compounds having this relation are rarely obtained by direct substitution. Chlorine and its congeners, as we have already noticed, constitute the radicles of an important class of acids, but as all these compounds are essentially mon-hydric, and as chloro-substitution is well manifested in polyhydric acids only, we have usually no difficulty in distinguishing between chlorine, the independent acid-radicle, and chlorine the representative of hydrogen. It must be understood that many acids have a much more complex constitution than any to which we have as yet alluded.

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(21) ANHYDRIDES. — The ternary or oxacids are capable of yielding, by the direct or indirect loss of water, certain compounds known as anhydrides, or anhydrous acids. The reaction of mono- and polybasic acids to form anhydrides may be illustrated as follows: —

	Acids.			=	Anhydrides.
Periodic	$2HIO_4$	—	H_2O	=	I_2O_7
Sulphuric	$2H_2SO_4$	—	$2H_2O$	=	S_2O_6 or $2SO_3$
Phosphoric	$2H_3PO_4$	—	$3H_2O$	=	P_2O_5
Silicic	$2H_4SiO_4$	—	$4H_2O$	=	Si_2O_4 or $2SiO_2$

It is observable that the reactions in the case of bi- and tetrabasic acids may be preferably written thus:—

$$H_2SO_4 - H_2O = SO_3$$
$$H_4SiO_4 - 2H_2O = SiO_2$$

These equations, moreover, are thought to be the most correct, so that two atoms of a mono- or tribasic, and only one atom of a bi- or tetrabasic acid, are required to furnish single atoms of their respective anhydrides. Most of the anhydrides unite with water to form acids, all of them with basylous metallic oxides to form salts. Thus, CO_2 carbonic anhydride, and KHO hydrate of potassium, form $KHCO_3$ acid carbonate of potassium. Sometimes the distinction between an anhydride and its acid is very marked, as is also the conversion of one into the other; at other times it is difficult to distinguish between the moist anhydride and the acid. The dry anhydrides, whether solid, liquid, or gaseous, do not affect blue litmus paper; neither do the aqueous solutions of those few anhydrides that can dissolve in water without forming acids. The anhydrides have the property of attaching themselves to normal salts, to form compounds known as anhydro-salts. Thus we have $K_2Cr_2O_4$ chromate of potassium; and $K_2Cr_2O_4.Cr_2O_3$, or $K_2Cr_4O_7$ anhydro-bichromate of potassium; and $K_2Cr_2O_4.2Cr_2O_3$, or $K_2Cr_6O_{10}$ anhydro-terchromate of potassium. The property of forming anhydro-salts is confined almost entirely to the anhydrides of the polybasic acids.

(22) ALDEHYDS. — Common or acetic aldehyd C_2H_4O, is obtained by the oxydation or dehydrogenisation of alcohol C_2H_6O, whence its name aldehyd, from *alcohol dehydrogenatus*. The term is now applied to a class of bodies which have the same relation to their respective oxacids, that common aldehyd has to acetic acid. By oxydation, the aldehyds become converted into acids; and accordingly as the acids to which they pertain are monobasic, bibasic, or tribasic, so do they undergo the aforesaid conversion by the assumption of one, two, or three atoms of

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oxygen. Thus monobasic acetic acid $C_2H_4O_2$, results from common aldehyd C_2H_4O, by the absorption of one atom of oxygen. Normal aldehyds are not a very numerous or widely distributed class of compounds; but their chloro-derivatives are much more important. These chlor-aldehyds may be made from the normal aldehyds by direct substitution of chlorine for hydrogen, but are preferably obtained from other sources by several indirect processes. The chlor-aldehyds react with water to exchange chlorine Cl, for peroxide of hydrogen HO, so as to form chlorhydric acid, and the normal oxacids to which they correspond: —

	Chlor-aldehyds.							Acids.
Nitric	$ClNO_2$	+	H_2O	=	HCl	+	HNO_3	$(HO)\ NO_2$
Sulphuric	Cl_2SO_2	+	$2H_2O$	=	$2HCl$	+	H_2SO_4 or	$(HO)_2\ SO_2$
Phosphoric	Cl_3PO	+	$3H_2O$	=	$3HCl$	+	H_3PO_4	$(HO)_3\ PO$

It is observable that the conversion of normal aldehyds into acids by oxydation, may be represented as an exchange of hydrogen H, for peroxide of hydrogen HO, analogous to the above-illustrated exchange of chlorine for peroxide of hydrogen. Thus the reactions of chloro- and normal acetic aldehyds, upon water and peroxide of hydrogen respectively, may be written in the following corresponding manners: —

$$\left.\begin{array}{l} Cl\,.\,C_2H_3O + \left\{\begin{matrix} H \\ HO \end{matrix}\right. = \left\{\begin{matrix} H \\ Cl \end{matrix}\right\} + HO\,.\,C_2H_3O \\ H\,.\,C_2H_3O + \left\{\begin{matrix} HO \\ HO \end{matrix}\right. = \left\{\begin{matrix} HO \\ H \end{matrix}\right\} + HO\,.\,C_2H_3O \end{array}\right\} \text{ or } C_2H_4O_2$$

The chlor-aldehyds bear to their corresponding acids, the same relations that metallic chlorides bear to metallic hydrates, and may be represented accordingly, thus: —

Chlorides.	Chlor-aldehyds.	Hydrates.	Acids.
$Zn'\ Cl$	$\left\{\begin{matrix} (C_2H_3O)'\ Cl & \text{Acetic} \\ (NO_2)'\ Cl & \text{Nitric} \end{matrix}\right.$	$Zn'\left\{\begin{matrix} H \end{matrix}\right\}O$	$\left\{\begin{matrix} \left\{\begin{matrix} (C_2H_3O)' \\ H \end{matrix}\right\}O & \text{Acetic} \\ \left\{\begin{matrix} (NO_2)' \\ H \end{matrix}\right\}O & \text{Nitric} \end{matrix}\right.$
$Pt''\ Cl_2$	$(SO_2)''Cl_2$ Sulphuric	$Pt''\left\{\begin{matrix} H_2 \end{matrix}\right\}O_2$	$\left\{\begin{matrix} (SO_2)'' \\ H_2 \end{matrix}\right\}O_2$ Sulphuric
$Bi'''Cl_3$	$(PO)'''\ Cl_3$ Phosphoric	$Bi'''\left\{\begin{matrix} H_3 \end{matrix}\right\}O_3$	$\left\{\begin{matrix} (PO)''' \\ H_3 \end{matrix}\right\}O_3$ Phosphoric

as if the molecular groupings, C_2H_3O, NO_2, SO_2, PO, &c., were like zinc, platinum, bismuth, &c., proto-, bi-, and ter-equivalent respectively.

(23) AMIDES. — Compounds formed on the type of one or more molecules of ammonia, in which some, or all, of the hydrogen

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atoms have been replaced by equivalent substitution, constitute the amides. Precisely as we have chlorides and hydrates of molecular groupings analogous to chlorides and hydrates of the elements, so have we amides of molecular groupings analogous to amides of the elements. We may adduce the following as examples: —

$\left.\begin{matrix}K'\\H\\H\end{matrix}\right\}$N Potassamide	$\left.\begin{matrix}(C_2H_3O)'\\H\\H\end{matrix}\right\}$N Acetamide	$\left.\begin{matrix}(C_2H_5)'\\(C_2H_5)'\\(C_6H_5)'\end{matrix}\right\}$N Diethyl-phenylia.
$\left.\begin{matrix}Pt''\\H_2\\H_2\end{matrix}\right\}N_2$ Diplatin-amide	$\left.\begin{matrix}(SO_2)''\\H_2\\H_2\end{matrix}\right\}N_2$ Sulphamide	$\left.\begin{matrix}(CS)''\\(C_3H_5)'H\\H_2\end{matrix}\right\}N_2$ Thiosin-amine.
$\left.\begin{matrix}Bi'''\\H_3\\H_3\end{matrix}\right\}N_3$ Bismuth-amide ?	$\left.\begin{matrix}(PO)'''\\H_3\\H_3\end{matrix}\right\}N_3$ Phosphamide	$\left.\begin{matrix}(C_6H_5O_4)'''\\(C_6H_5)'_3\\H_3\end{matrix}\right\}N_3$ Triphenyl-citramide.

We have an infinite variety of other and much more complex amides, diamides, triamides, &c., in which some, or all, of the hydrogen atoms are replaced by very numerous and varied mono-, bi-, ter-, &c., equivalent elements or groupings.

(24) COMPOUND RADICLES. — Not only may the above-adduced, and other similar molecular groupings, be considered as the equivalents of one or more atoms of hydrogen in the types chloride, hydrate, and amide, and in the indefinite number of more special types, but they are actually introduced into these different compounds in exchange for one or more atoms of hydrogen or of its representatives: —

Chlorid-ethyl . $C_2H_5.Cl + \left.\begin{matrix}K\\H\end{matrix}\right\}O = KCl + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$ Alcohol.

Iodid-amyl . . $C_5H_{11}.I + \left.\begin{matrix}C_2H_5\\K\end{matrix}\right\}O = KI + \left.\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}\right\}O$ Ethylate of amyl.

Alcohol . . . $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + H_2SO_4 = \left.\begin{matrix}H\\H\end{matrix}\right\}O + C_2H_5.HSO_4$ Sulphovinic acid.

Chloride of benzoyl $C_7H_5O.Cl + \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N = HCl + \left.\begin{matrix}C_7H_5O\\H\\H\end{matrix}\right\}N$ Benzamide.

Citric ether $\left.\begin{matrix}(C_6H_5O_4)'''\\(C_2H_5)'_3\end{matrix}\right\}O_3 + 3\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N = 3\left|\begin{matrix}H\\(C_2H_5)'\end{matrix}\right\}O + \left.\begin{matrix}(C_6H_5O_4)'''\\H_3\\H_3\end{matrix}\right\}N_3$ Citramide.

By compound radicles are understood those molecular groupings, whether or not isolable, which have been, or which may be, transferred from one compound to another in exchange for one or more atoms of hydrogen, or of its representatives. The different

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compound radicles that we have alluded to in the foregoing sections, all belong to one or other of two principal classes, which indeed comprise the great majority of compound radicles. We have in the first place proto-, bi-, and ter-equivalent radicles produced from monobasic, bibasic, and tribasic oxygen-acids, by the abstraction of one, two, or three atoms respectively of peroxide of hydrogen; or from the corresponding aldehyds by the abstraction of one, two, or three atoms of hydrogen; or from the corresponding chlor-aldehyds by the abstraction of one, two, or three atoms of chlorine. To this class belong the radicles C_2H_3O' acetyl or othyl, NO_2'nitryl, SO_2''sulphuryl, PO'''phosphoryl, $C_6H_5O_4'''$ citryl, &c. Secondly, we have proto-, bi-, ter-, &c., equivalent radicles resulting from binary hydrogenised bodies by the abstraction of one, two, three, or more atoms of hydrogen respectively. The radicles obtained in this manner from hydrocarbons can also result from their corresponding chlor-hydrocarbons by the abstraction of one, two, or three atoms of chlorine; and from their corresponding mon-atomic, bi-atomic, and ter-atomic, alcohols or hydrates, by the abstraction of one, two, or three atoms of peroxide of hydrogen. Taking the hydrocarbon C_2H_6 as an illustration, we have the radicles C_2H_5' ethyl, C_2H_4''ethylene, C_2H_3'''glycyl, &c., thus: —

Prot-equivalent.	Bi-equivalent.	Ter-equivalent.
C_2H_5' H	C_2H_4'' H_2	C_2H_3''' H_3
C_2H_5' Cl	C_2H_4'' Cl_2	C_2H_3''' Cl_3
C_2H_5', H } O	C_2H_4'', H_2 } O_2	C_2H_3''', H_3 } O_3
C_2H_5', H, H } N	C_2H_4'', H_2, H_2 } N_2	C_2H_3''', H_3, H_3 } N_3

Binary hydrogenised bodies yield as many radicles as they contain atoms of hydrogen, and the equivalency of the radicle increases by one unit for every atom of hydrogen abstracted, as illustrated below in the case of our primary types.

Prot-equivalent Radicles.	Bi-equivalent Radicles.	Ter-equivalent Radicles.	Tetr-equiv. Radicles.
$HCl-H=Cl'$ Chlorine.			
$H_2O-H=HO'$ Eurhyzene.*	$H_2O-H_2=O''$ Oxygen.		
$H_3N-H=H_2N'$ Amidogen.	$H_3N-H_2=HN''$ Imidogen.	$H_3N-H_3=N'''$ Nitrogen.	
$H_4C-H=H_3C'$ Methyl.	$H_4C-H_2=H_2C''$ Methylene.	$H_4C-H_3=HC'''$ Formyl.	$H_4C-H_4=C''''$ Carbon.

* Eurhyzene, a name proposed by Laurent for the radicle peroxide of hydrogen.

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(25) DOUBLE DECOMPOSITION.—Although the radicles conceived to enter into the composition of many bodies have not necessarily any separate existence therein, apart from the other constituents, yet they are not altogether imaginary, for they represent distinct groupings of elements, which are capable of being transferred to other compounds by means of double decomposition. There is no proof, for instance, that alcohol C_2H_6O, contains preformed, the radicle ethyl C_2H_5; but by attributing to alcohol the formula $C_2H_5.HO$ we imply that, in many double decompositions, the grouping C_2H_5 is capable of being transferred from alcohol to some other body in exchange for hydrogen or its representatives, thus: $HCl + C_2H_5HO = C_2H_5Cl + HHO$. By means of the above-described two classes of compound radicles, we are enabled to refer the great majority of hydrocarbons, chlorhydrocarbons, aldehyds, and chlor-aldehyds to the type of one or more atoms of chlorhydric acid, and the alcohols, ethers, oxacids, and oxysalts, to the type of one or more atoms of water; while by far the largest proportions of the reactions of these bodies upon one another, and upon bodies belonging to other types, may be regarded as instances of that normal double decomposition to which we have already alluded, in which the types of the reacting and resulting bodies are the same. Double decomposition, or the mutual interchange of atoms or groupings, of which several examples are afforded in the preceding section, appears indeed to be the primary type of chemical action. We shall hereafter see that the direct union of two elements, the substitution of one element for another, the breaking up of a compound into its elements, and the liberation of a single element in the free state, may all be looked upon as instances of double decomposition. The production of a free element by double decomposition corresponds exactly with the production of a free radicle, as shown in the two following equations: —

$$HCl + HCu_2 = Cu_2Cl + H_2$$
$$C_2H_5Cl + C_2H_5Zn = ZnCl + C_4H_{10}$$

(26) DIAMERONES. — Bodies containing two distinct separable compound radicles transferable by double decomposition, were termed by Laurent diamerones. These bodies contain necessarily the residues of the two compounds from which they were produced, and under certain circumstances can regenerate those compounds. The distinctive character of a diamerone is its capability of directly or indirectly taking up the elements of water, and of thereby form-

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ing two simpler bodies from which it was, or might have been, produced. Benzoic ethyl, for instance, is a diamerone: it contains indubitably a benzoic residue or radicle, and an ethylic residue or radicle, both transferable by double decomposition. By its reaction with water it breaks up into a benzoic compound, namely, benzoic acid $C_7H_6O_2$, and an ethylic compound, namely, alcohol C_2H_6O; the two substances from which it either was, or might have been, produced: —

$$C_7H_5(C_2H_5)O_2 + HHO = C_7H_5HO_2 + C_2H_5HO.$$

The formulæ of diamerones, though variously modified by different chemists, always indicate the dual nature of the bodies. A diamerone is most usually formulated in relation to one or other of the general types, or to the special type of the most chlorous of the bodies from which it was obtained. Thus benzoic ethyl may be referred either to the water type H_2O, or to the benzoic acid type $C_7H_6O_2$, and may be written $\left.\begin{matrix}C_2H_5\\C_7H_5O\end{matrix}\right\}O$ or $C_7H_5(C_2H_5)O_2$. We may obtain diamerones of any conceivable degree of complexity, but the building up and breaking up are essentially dual in character. Thus from benzoic acid and nitric acid we may obtain the diamerone nitrobenzoic acid $C_7H_5(NO_2)O_2$; and from nitrobenzoic acid and alcohol we may obtain the more complex diamerone, nitrobenzoic ether, $C_7H_4(NO_2)(C_2H_5)O_2$; which under certain circumstances can regenerate alcohol and nitrobenzoic acid; the last-mentioned body, moreover, being able to regenerate benzoic and nitric acids.

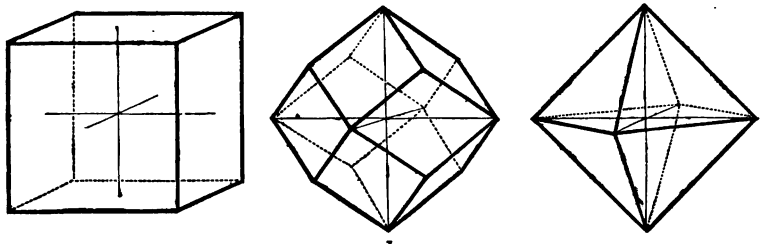
Unitary bodies, such, for instance, as alcohol, benzoic acid, ammonia, benzine, &c., and their derivatives by elementary substitution, were termed by Laurent *aplones*. None of these bodies can yield two distinct separable compound radicles, unless indeed peroxide of hydrogen be taken for one of them.

(27) Crystallisation. — Solid bodies occur either in the amorphous or the crystalline state. Crystalline bodies are characterised by certain well defined geometrical forms, bounded nearly always by plane surfaces. Crystallographers have distributed the multitudinous forms of crystals into six primary classes or systems, distinguishable from one another by the relative positions and lengths of the three axes about which the planes are arranged; while the different figures of any particular system are distinguishable by the arrangement of the planes in respect to the axes. Thus the cube or hexahedron, the rhombic dodecahedron, and the octahedron, all belong to the regular system, which is characterised by three equal

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axes cutting one another at right angles (*fig.* 1). But in the cube (*a*) each plane cuts one axis, and is parallel to two; in the dodecahedron (*b*) each plane cuts two axes, and is parallel to the third; while in the octahedron (*c*) each plane cuts the three axes.

Fig. 1.



a *b* *c*

The names and definitions of the six crystalline systems are shown in the accompanying table:

1. Regular system	The three axes equal and rectangular.
2. Square prismatic — Two equal axes 3. Right prismatic — All unequal	The three axes unequal and rectangular.
4. Rhombohedral	The three axes equal but not rectangular.
5. Oblique prismatic — One rectangular to two 6. Doubly oblique prismatic — None rectangular	The three axes not equal nor rectangular.

The three axes of the rhombohedral system are equal, occur in different planes, and cross at equal angles. The three axes of the oblique and doubly oblique systems are all unequal. In the singly oblique system, one axis is rectangular to the two others, but the principal axis is oblique to the plane of the rectangular and remaining oblique axes.* All the systems exhibit certain comparable forms, in which the planes bear corresponding relations to their respective axes. Thus we have the following analogues (*fig.* 2):

* Dr. Leeson's classification of crystalline forms into nine groups, as shown below, although not generally adopted, is very exact and intelligible: —

Rectangular, Equiaxial (*Regular*).	Binequiaxial (*Square prismatic*).	Inequiaxial (*Right prismatic*).
Oblique Rectangular, Equiaxial.	Binequiaxial.	Inequiaxial (*Oblique prismatic*).
Oblique, Equiaxial (*Rhombohedral*).	Binequiaxial	Inequiaxial (*Doubly oblique*).

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Fig. 2.

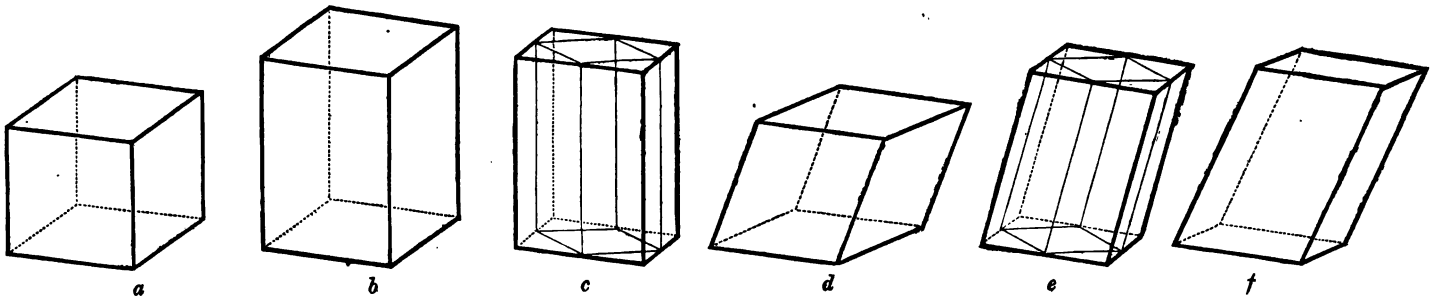
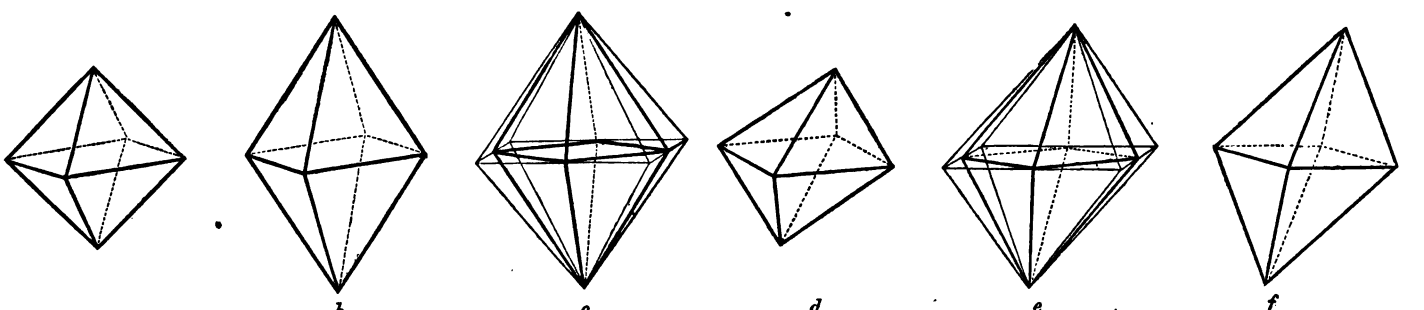


Fig. 3.



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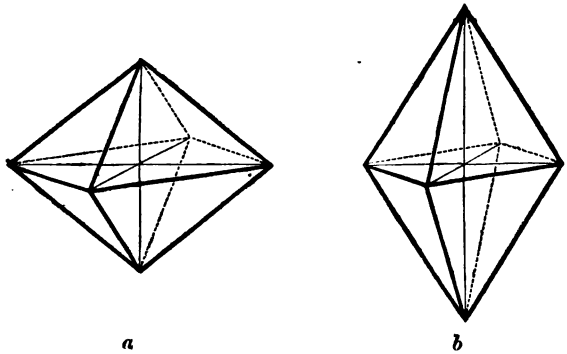
a the cube, *b* the square prism, *c* the right rectangular and right rhombic prism, *d* the rhomboïd, *e* the oblique rectangular and oblique rhombic prism, *f* the doubly oblique prism.

Again (*fig.* 3), we have *a* the regular octahedron, *b* the square octahedron, *c* the right rectangular and right rhombic octahedron, *d* the rhomboïdal octahedron, *e* the oblique rectangular and oblique rhombic octahedron, *f* the doubly oblique octahedron.

The right prismatic and oblique prismatic systems, it is observable, yield two very distinct varieties of prism and octahedron, accordingly as the planes are arranged to cut one or two of the axes, and thereby to produce a rectangular or a rhombic base, thus, ; but this double relation of the planes to the axes exists also in the other systems, though the corresponding crystals cannot be so easily discriminated.

The forms belonging to different crystalline systems shade off into one another by insensible gradations. Thus, the differences between the regular and the square prismatic systems depend upon the circumstance that, while in the regular system all three axes are equal, in the square system one of the axes is longer or shorter than the other two: and when this unequal axis is but very little longer or shorter, we obtain square prisms and square octahedrons, approximating very closely to the cube and regular octahedron. Again, in the regular system, the three equal axes cut one another at right angles, *i. e.* angles of 90°; and when the equal axes of the rhombohedral system cut one another at angles of 89° 30′ and 90° 30′, we obtain rhombohedral forms scarcely distinguishable from those of the regular system; and so in many other cases. Crystals belonging to different systems, however, are distinguishable, not only by their external forms, but by their

Fig. 4.



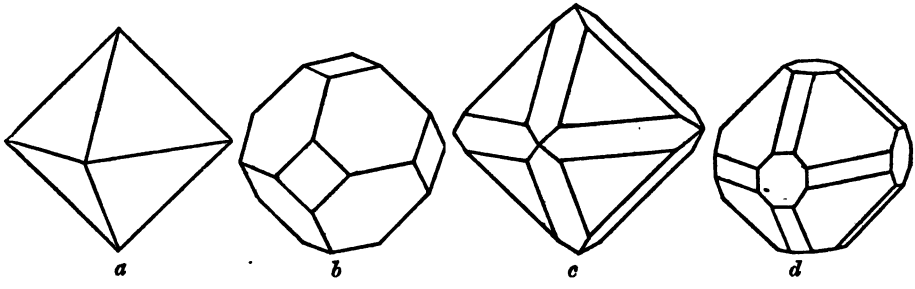
a *b*

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different relations to light and heat. It is observable in the regular system, that all simple crystals of the same genus, the octahedron for instance, have the same shape; while in the other systems we have very differently shaped octahedrons, &c., according to the relative lengths and angular inclinations of the axes. Thus an obtuse, and an acute octahedron, both belonging to the square prismatic system, are shown in *fig.* 4.

(28) COMPOSITE AND HEMIHEDRAL FIGURES. — Crystalline forms are either simple or composite, primary or secondary. Composite forms have two or more varieties of faces, the secondary faces resulting from the replacement of the edges or solid angles of the primary form by the faces of some other form. Thus, an octahedral crystal of alum usually has its angles replaced by planes of the cube, and its edges by planes of the rhombic dodecahedron (*fig.* 5).

Fig. 5.

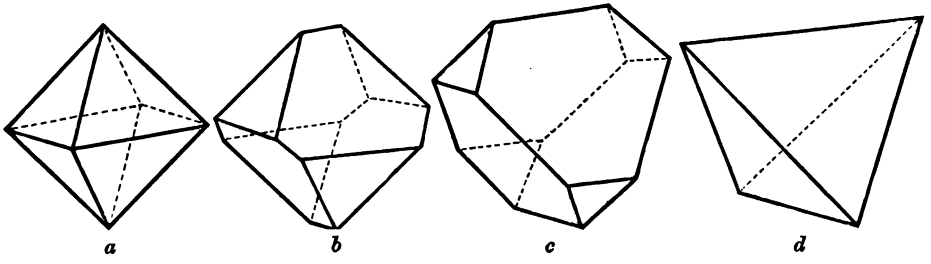


In the regular system, all the edges and angles must be modified in the same manner; in the square system, the terminal edges or angles are modified differently from the lateral edges or angles; while in the right system, not only are the terminal edges or angles modified differently from the lateral, but the alternate lateral edges or angles are modified differently from one another. The secondary forms of the three oblique systems present a still greater degree of complexity, and especially those of the doubly oblique system, in which all symmetry appears to be lost.

Forms which result from the development of one set of faces, to the detriment, and finally to the disappearance of a similar set, are termed hemihedral. Thus in a regular octahedron (*fig.* 6, *a*), four alternate faces are frequently developed at the expense of the other four, which may ultimately vanish altogether, leaving a four-sided hemihedral figure, namely, the regular tetrahedron (*d*).

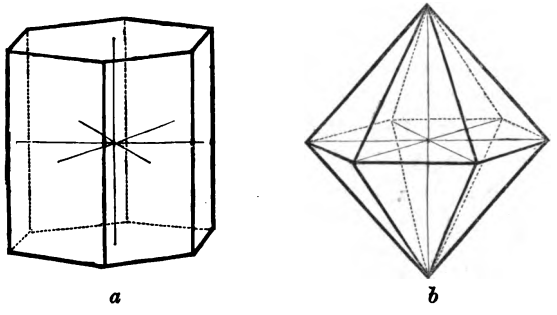
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Fig. 6.



Some crystallographers have referred the forms of the rhombohedral system to four axes, three equal, in the same plane, and crossing at angles of 60°, the fourth unequal and perpendicular to the plane of the other three. According to this view, the hexagonal prism (*fig.* 7, *a*) must be regarded as a principal figure, and the rhomboïd as a hemihedral modification of the pyramidal dodecahedron (*b*).

Fig. 7.



(29) Isomorphism. — The same substance usually affects one particular crystalline form, but may frequently be obtained in two or more convertible forms belonging to the same system. Thus common salt usually crystallises in cubes, but may be obtained in octahedrons. Moreover, a substance may crystallise in an indefinite number of secondary forms: calc-spar, for instance, crystallises in above six hundred secondary forms of the rhombohedral system. But not only does a substance affect one or more forms belonging to a particular system, but the solid angles and edges of its crystals have a determinate and almost invariable relation to one another, dependent, of course, upon the length and inclination of the crystalline axes. Mitscherlich's doctrine of isomorphism affirms that bodies having a similar chemical constitution, or, as he ex-

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pressed it, "the same number of atoms combined in the same way," have the same crystalline form, as determined by the measurement of their angles. Thus corresponding phosphates and arseniates; sulphates, seleniates, manganates, and chromates; protosalts of magnesium, zinc, cadmium, manganese, iron, nickel, cobalt, and copper; sesquisalts of iron, aluminum, chromium, and manganese; &c.; are strictly isomorphous. Of course hydrated salts are comparable only when they contain the same number of atoms of water of crystallisation. Bodies having apparently an exactly similar constitution are not necessarily isomorphous, but are rather divisible into two or more groups, of which the respective members are isomorphous: thus we have the magnesian family of carbonates crystallising in rhomboïds, and the strontian family crystallising in right rhombic prisms. On the other hand, the possession of an equal number of atoms is not essential to isomorphism, for two atoms of one element are not unfrequently isomorphous with one atom of another element; and sometimes a molecular grouping, NH_4 or ammonium, for instance, is isomorphous in its combinations with an elementary atom, that of potassium, for instance.

The corresponding angles of isomorphous bodies are not always precisely equal, but may differ from each other by one or two degrees. This discrepancy, however, is rendered unimportant by the circumstance, that the angles of different crystals of one and the same substance can present similar variations, by the agency of certain modifying causes.

The isomorphism of bodies in any other than the regular system is a most valuable indication of similarity in molecular composition. Elements belonging to the same natural families are frequently isomorphous, and especially yield analogous isomorphous compounds. The majority of the metals crystallise in the regular system. An isomorphism in this system, of bodies not possessing obvious analogies, is unimportant from the fact already noticed, that regular crystals of the same genus cannot have any variations in their angles. But even in other systems, we do occasionally meet with isomorphous substances, in which no similarity of composition can be traced.

By evaporating a solution of two different salts that are not isomorphous, we obtain separate crystals of each salt, that may readily be distinguished from one another. But the solution of two or more isomorphous salts generally yields homogenous crystals of the isomorphous salts mixed in indefinite proportions. Thus a solution containing both chrome alum, and common alum deposits

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perfect octahedra, containing chromium and aluminum, mixed in any proportion. The formula of the mixed salt has to be written $K(Al\text{-}Cr)^2(SO_4)_2$. Many natural minerals are remarkable for a similar isomorphous mixture or replacement of their metallic constituents.

(30) POLYMORPHISM.—Some substances are found to crystallise in two incompatible forms, that is, in forms belonging to two different systems: such substances have been termed dimorphous. It has been noticed by Laurent, and particularly by Pasteur, that the forms of dimorphous crystals almost always occur near the boundary lines, as it were, of the two systems. The two forms of crystallised sulphur, carbonate of calcium, arsenious anhydride, iodide of mercury, &c., are mutually related in this manner. We have already seen that the crystals of some particular substance may present corresponding angles, differing by two or three degrees; and such an amount of angular difference in boundary crystals, would be quite sufficient to transfer them from one system to another.* Dimorphism frequently enables us to recognise an isomorphism that would otherwise be overlooked. Thus potassium and sodium salts are for the most part isomorphous, but nitrate of potassium usually crystallises in right rhombic prisms, and nitrate of sodium in rhomboïds. It appears, however, that each salt can crystallise in both systems, and that the corresponding forms are isomorphous. The two salts are, in fact, iso-dimorphous, only that nitrate of potassium most commonly affects the one form, and nitrate of sodium the other. The carbonates of lead and calcium are iso-dimorphous in a similar manner, the ordinary form of the one corresponding to the rare form of the other. Some few bodies, titanic acid for instance, are trimorphous. According to Mitscherlich, the sulphates and seleniates of zinc are iso-trimorphous.

(31) ALLOTROPY. — Certain bodies, both elementary and compound, are capable of existing in two or more different states, distinguished from one another by important variations of their physical and chemical properties. Dimorphism is only a special instance of this more general phenomenon of allotropy. The three principal states in which the same solid body can exist are known as the crystalline, vitreous, and amorphous respectively;

* According to Laurent, bodies are isomorphous when they present the same or very nearly the same, axes and angles, no matter to what different systems the comparable forms belong.

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but of these there are many minor modifications. A very good instance of allotropy is furnished us by phosphorus. This element may be obtained crystallised in octahedrons or in rhombic dodecahedrons; but it usually occurs in flexible, transparent, yellowish white, waxy-looking sticks, of specific gravity 1·85, which melt at a temperature of 44·5°, inflame when merely exposed to the sun or warm air, and dissolve readily in bisulphide of carbon. But if phosphorus, out of access of air, be heated for many hours at a temperature of 240–50°, it becomes converted into a bright red-coloured brittle mass, of specific gravity 2·1, which is insoluble in bisulphide of carbon, does not melt unless heated to 250°, or inflame, save at a somewhat higher temperature, when it becomes reconverted into the vitreous variety. Other intermediate conditions are also known. Several of the elements present similar differences: thus carbon occurs in at least three distinct allotropic conditions, as instanced by diamond, graphite, and charcoal. Sulphur occurs crystalline in two systems, also in a viscid, and in a pulverulent or amorphous state. Among compound bodies, sulphide of mercury is either black or scarlet, and sulphide of antimony either grey or orange. Even ordinary glass, the perfection of a vitreous compound, may be obtained in an opaque semi-crystalline condition, known as Réaumur's porcelain. As a general rule, allotropic modifications of the same substance are formed at different temperatures, and the transition from the one state into the other is attended with an evolution or absorption of heat. Hitherto allotropic modifications of the same element have rarely been traced satisfactorily into distinct series of compounds; but Brodie has of late succeeded in producing several compounds of carbon, in which the carbon evidently exists in the state of graphite.

(32) ISOMERISM. — Dimorphic and other allotropic modifications of the same substance are for the most part readily convertible into one another. But we are acquainted with a great number of essentially different compounds which have exactly the same centesimal composition, and are not, as a rule, mutually convertible. Such bodies are termed isomeric. A particular form of isomerism, known as polymerism, is instanced particularly by certain hydrocarbons: —

Ethylene	$C_2 H_4$	= 2 vol.
Propylene	$C_3 H_6$	= 2 vol.
Butylene	$C_4 H_8$	= 2 vol.
Amylene	$C_5 H_{10}$	= 2 vol.
Cetylene	$C_{16} H_{32}$	= 2 vol.

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In all the above bodies, the ratio of hydrogen to carbon is the same, but the quantities of both elements contained in the respective two-volume molecules vary greatly, although by a regular sequence. Moreover, in ethylene, for example, we cannot replace a smaller quantity than one fourth, but in amylene we can replace one tenth of the hydrogen. Other compounds are what is termed metameric. Thus, formate of ethyl and acetate of methyl have precisely the same centesimal composition; and with the same number of atoms correspond to the same volume. But we know that the two bodies differ in their intimate constitution; that the one contains a formic and an ethylic group, and can break up into a formic and an ethylic compound; while the other contains an acetic and a methylic group, and can break up into an acetic and a methylic compound, as indicated in their respective formulæ: —

$$C\ H\ (C_2H_5)\ O_2 \text{ Formate of ethyl,}$$
$$C_2H_3\ (C\ H_3)\ O_2 \text{ Acetate of methyl.}$$

To these bodies may be added propionic acid, $C_3H_6O_2$, a substance which is not dual in its nature, or does not contain its carbon in two distinct transferable groupings. In many cases we can at present only speculate on the nature of the isomerism. Thus the formula $C_7H_6O_2$ represents the two-volume molecule of salicylic aldehyd, and also that of benzoic acid, two very different substances, which are neither of them diamerones, but contain their carbon under one single form.

(33) Atomic volume. — The volume occupied by any given proportion of a substance will, of course, be directly as the quantity, and inversely as the density of that substance. Hence the relative volumes occupied by atomic proportions of different substances, are found by dividing their atomic weights by their specific gravities; thus, $\frac{\text{atomic weight}}{\text{specific gravity}} = \text{atomic volume}$. By this means we have already ascertained that the atomic volumes of compound gases are to those of simple gases as two to one.

In determining the atomic volumes of solid and liquid substances, it has been customary to refer their specific gravities to that of water as unity, and their atomic weights to that of oxygen as 100; such being the standards adopted by chemists who have worked most on the subject. The atomic volumes of bodies are necessarily independent of the standards adopted; only that with different standards the ratios would be expressed by different

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numbers. The atomic volumes of solid and liquid bodies have not been found to present any very simple relations to one another, but nevertheless some generalities have been arrived at. Isomorphous elements, in particular, have frequently the same atomic volume, as instanced by the metals iron, manganese, cobalt, nickel, and copper, all of which have the number 44. Kopp has shown that under certain definite conditions the atomic volumes of homologous liquids increase by 275 for every increment of CH_2; and that the atomic volumes of metameric liquids are sensibly equal.

The atomic volume of a salt may be looked upon as the sum of the volume of the metal, plus that of the remaining constituents. Thus the atomic volumes of the metals lead and silver are 114 and 130 respectively; and the atomic volumes of the nitrates of lead and silver, 472 and 488 respectively; so that

$$\begin{aligned} PbNO_3 \text{ or } 472 - Pb \text{ or } 114 &= NO_3 \text{ or } 358, \\ \text{and } AgNO_3 \text{ or } 488 - Ag \text{ or } 130 &= NO_3 \text{ or } 358. \end{aligned}$$

Hence we assume 358 as the atomic volume of the residue NO_3. If we now proceed to the nitrates of strontium and barium, we find that their atomic volumes are 466 and 501 respectively, and deducting 358 for the value of the nitric residue, we have

$$\begin{aligned} SrNO_3 \text{ or } 466 - NO_3 \text{ or } 358 &= Sr \text{ or } 108, \\ \text{and } BaNO_3 \text{ or } 501 - NO_3 \text{ or } 358 &= Ba \text{ or } 143. \end{aligned}$$

It is found that the atomic volumes of strontium and barium salts may be well explained by, according to the respective metals, the above atomic volumes. The atomic volumes ascertained in this manner, are termed saline volumes, and those obtained by taking the specific gravities of the elements, primitive volumes. In a few cases only, it is found that the atomic volume of a free element differs from the volume which it has in combination; or that its primitive, differs from its saline volume. The determination of atomic volumes depends upon the observation of specific gravities, and as specific gravity varies with temperature and allotropic condition, it is evident that the volume results calculated therefrom can be only approximative. The details of this subject will be considered hereafter, but it was necessary at starting to explain that the relative bulks of atomic proportions of different bodies constitute their atomic volumes.

(34) ATOMIC HEAT.— Inasmuch as a pint of boiling water is quite as hot as a quart of boiling water, it is evident that the

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temperature of a body does not afford any criterion of the amount of heat that it contains. Again, a pound of water will absorb twenty-three times as much heat as will a pound of mercury, in arriving at the same degree of temperature. The relative quantities of heat, or the specific heats, of different bodies are ascertained by determining the amounts of heat which equal weights evolve, when cooled from one given temperature to another, the amount of heat evolved being measured by the quantity of ice that can be melted by its action, or by other similar means. The specific heat of water, which is found to exceed that of any other liquid or solid, is taken as the standard of comparison or unity. If instead of taking equal weights of different substances, we take proportional atomic weights, we obtain the atomic heats, or the relative quantities of heat which the atoms of different substances evolve or absorb by a given change of temperature. The specific heats of gaseous bodies are still *sub judice;* but the other elements may be divided, as regards their specific heats, into two groups. In the members of each group, the specific heats are inversely as the atomic weights; but the product of the specific heat into the atomic weight, or the atomic heat, gives in one group the constant 3, and in the other group the constant 6. The specific heats of the members of one class of compound bodies are not comparable with those of the members of another class, but are readily comparable *inter se,* so that, as aphorised by Regnault, "in all compound bodies of the same atomic composition, and of similar chemical constitution, the specific heats are inversely as the atomic weights." Thus the atomic heat of the nitrates gives the constant 24, that of the sesquioxides 27.

(35) DIFFUSION AND COLLECTION OF GASES. — Some liquids mix with one another, and others do not, as is well known, but all gases and vapours mix readily with one another. If coloured water be poured carefully on to a solution of common salt, the water, being lighter than the brine, will float on the top; and if the vessel be kept in a quiet situation, the two layers of liquid may be preserved comparatively unmixed for several weeks. By a little management, a heavy liquid may be poured through a lighter liquid, water through alcohol for instance, without much admixture taking place; and conversely, into a jar filled with water, and inverted with its mouth under water, alcohol may be passed or poured upwards through the water so as to occupy the upper part of the jar. Gases may be poured downwards or upwards through one another in a similar manner. Thus, if a cylindrical jar be

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held under the orifice of a tube conveying carbonic acid, which is a very heavy gas, the carbonic acid will fall through the air to the bottom of the jar, and gradually accumulating, will ultimately displace all the air, and occupy the entire jar. Conversely, if an inverted cylindrical jar be held over the orifice of a tube conveying hydrogen, which is a very light gas, the hydrogen will pass upwards through the air to the top of the cylinder, and gradually accumulating, will ultimately displace all the air and fill the jar. These two modes of collecting gas by displacement of air, are termed, *par excellence*, the methods of displacement, downwards and upwards respectively. But gases have a very strong tendency to intermix or diffuse, so that if a jar of hydrogen be inverted upon a jar of carbonic acid, and the two be set aside, the hydrogen will not remain floating on the carbonic acid, like the water on the brine, but the heavy carbonic acid will gradually rise, and the light hydrogen gradually fall, until a complete diffusion of the two gases into each other has taken place. This mixture takes place with considerable force. If a tube, closed at one end with porous stucco, be filled with hydrogen, and inverted on to a vessel of mercury, the tendency of the hydrogen to mix with the external air by passing through the pores of the stucco is so great, that by its passage out, it will actually raise up a column of mercury two inches high, or in other words it will balance $\frac{1}{15}$ part of the atmospheric pressure. The details of diffusion will have to be subsequently considered; but it may be observed here, firstly, that every gas has its own special rate of diffusion, which is inversely proportional to the square root of its specific gravity; and secondly, that diffusion is always a process of interchange, the gas *A* diffusing into the gas *B*, and the gas *B* diffusing, though not to the same amount, into the gas *A*. Thus, in the stucco tube experiment, hydrogen passes out and air passes in; but more hydrogen goes out than air enters, as shown by the rise of the mercury in the tube. This strong tendency to admixture renders the collection of gases by displacement of air a process of limited applicability. In practice, it is always advisable to generate the gas somewhat quickly, to carry the delivery tube to the bottom or top of the receiver, according as the gas is heavy or light, and to partially close the mouth of the receiver with a glass plate or other contrivance.

But gases are usually collected, not by the displacement of air, but by the displacement of water or mercury. The jar or receiver is filled with water, and inverted with its mouth under water, in a

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large vessel termed the pneumatic trough, so that the water may be sustained in the inverted jar by atmospheric pressure. The delivery tube from the retort, flask, or bottle in which the gas is generated, dips into the water of the trough under the mouth of the jar, and the gas then bubbles up through the water in the jar, and gradually displaces the whole of it, so as entirely to fill the jar. Gases which are dissolved or decomposed by water, are collected in a similar manner over mercury, in the mercurial trough. The impurities often contained in different gases, when first generated, are removed by passing them through some liquid, or over a solid moistened with the liquid, or over some solid, by which the impurity is absorbed and retained. Thus, aqueous vapour is removed from a gas, by causing it to bubble through oil of vitriol contained in a U-tube or two-necked bottle, or over pumice moistened with oil of vitriol, or over chloride of calcium or quicklime — oil of vitriol, chloride of calcium, and quicklime being substances which have a great power of absorbing water or watery vapour.

§ II. Hydrogen.

Symbol, H; *Proportional number*, 1; *Density*, 1; *Atomic volume* □.

(36) It was doubtful whether hydrogen existed naturally in an uncombined or free state, until Bunsen recognised its presence, though in very variable proportions, in the gases evolved from the solfataras of Iceland. By its union with oxygen, it constitutes water, whence its name (ὑδῶρ γενναῶ), and in this form is extensively distributed through earth, air, and ocean. It is an essential ingredient of many inflammable minerals, such as coal, amber, and petroleum. It likewise exists, naturally, as a component of marsh gas or coal damp, ammonia, and sulphydric acid. It is an important constituent of all organised tissues and educts. It enters into the composition of many manufactured substances of great value and most varied character, such, for instance, as oil of vitriol, caustic soda, sal-ammoniac, vinegar, alcohol, wood spirit, &c. Hydrogen gas was discovered by Cavendish in the year 1766.

(37) Many chemical reactions liberate hydrogen from its com-

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binations. *a.* It is usually prepared by the action of metallic zinc upon diluted sulphuric acid: —

$$\overbrace{H_2SO_4}^{\text{Sulphuric acid.}} + Zn_2 = \overbrace{Zn_2SO_4}^{\text{Sulphate zinc.}} + H_2$$

Zinc granules or clippings, and sulphuric acid diluted with six or eight times its bulk of water, are placed in a bottle, the cork of which is fitted with a delivery tube of glass or vulcanised caoutchouc. Effervescence takes place immediately, and when the air originally contained in the bottle has been completely expelled, the unmixed gas may be collected over water in the pneumatic trough, or by upward displacement. Should the hydrogen be required absolutely pure, it must not only be prepared from zinc and acid as pure as can be obtained, but must also be passed through a solution of hydrate of potassium, to absorb any free acid, then through a solution of nitrate of silver to arrest any arsenic or sulphur, and lastly, through strong oil of vitriol, or over chloride of calcium, to free it from moisture.

Though in practice we always obtain our supply of hydrogen by the action of zinc or iron upon sulphuric or chlorhydric acid as above described, yet there are many other modes of generating the gas, some of which are highly interesting in a theoretic or scientific point of view, thus: — *β.* By passing steam over red hot iron turnings, usually disposed in a tube of iron, porcelain, or glass: —

$$\overbrace{2H_2O}^{\text{Water.}} + Fe_3 = \overbrace{Fe_3O_2}^{\text{Magnetic oxide iron.}} + H_4$$

γ. By introducing potassium or sodium up into an inverted tube or cylinder filled with water or alcohol, and standing in a vessel of the same liquid. It is advisable to wrap the metal in a piece of soft paper before plunging it under the mouth of the tube or cylinder: —

$$H_2O + Na = \overbrace{NaHO}^{\text{Hydrate sodium.}} + H$$

$$\overbrace{C_2H_6O}^{\text{Alcohol.}} + K = \overbrace{C_2KH_5O}^{\text{Ethylate potassium.}} + H$$

δ. By heating zinc or iron with a strong solution of hydrate of potassium or sodium: —

$$\overbrace{KHO}^{\text{Hydrate potassium.}} + Zn = \overbrace{KZnO}^{\text{Potassium zinc oxide.}} + H$$

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ε. By acting upon subhydride of copper with chlorhydric acid: —

Subhydride copper. Subchloride copper.

$$\overbrace{Cu_2H} + HCl = \overbrace{Cu_2Cl} + H_2$$

ζ. By heating formates or oxalates with excess of the hydrates of potassium, sodium, or calcium: —

Formate potassium. Carbonate potassium.

$$\overbrace{CKHO_2} + KHO = \overbrace{CK_2O_3} + H_2$$

Oxalate potassium.

$$\overbrace{C_2K_2O_4} + 2KHO = 2CK_2O_3 + H_2$$

η. By treating with hydrate of potassium, certain organic bodies having a tendency to form acids by oxidation: —

Benzoic aldehyd. Benzoate potassium.

$$\overbrace{C_7H_6O} + KHO = \overbrace{C_7KH_5O_2} + H_2$$

θ. By electrolysis of water, sulphuric acid, chlorhydric acid, &c: —

$$H_2O = O + H_2.$$

(38) Hydrogen being the lightest substance in nature, is conveniently taken as a standard for the specific gravity of gases: at mean pressure and temperature one centigramme of hydrogen occupies 1180 cubic centimetres.* It is 14·4 times lighter than atmospheric air, and about nine times lighter than the coal gas now substituted for hydrogen, on account of its cheapness, as a material for inflating air balloons. Soap bubbles blown with hydrogen ascend rapidly in the air; moreover, this gas may be easily poured upwards from one vessel into another. Hydrogen is very readily inflamed, even by a red hot wire or glass rod. When a lighted taper is passed up into an inverted jar of hydrogen, the gas burns quietly with a pale blue, scarcely visible flame, and the taper is extinguished. The flame takes place only at the line of demarcation between the hydrogen and external air. If the hydrogen is mixed with air or oxygen prior to its ignition, the flame takes place at once through the whole mass of gas, and is accompanied by a loud explosion. The most violent explosion occurs when two volumes of hydrogen are mixed with one volume of oxygen, or with five volumes of air. Hydrogen when pure is colourless, tasteless, inodorous, and, if diluted with air, may be breathed without inconvenience. At ordinary temperatures, water dissolves rather less

* One grain of hydrogen occupies 46·6 cubic inches.

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than 2 per cent. of its volume of hydrogen. It has never been liquefied.

Free hydrogen is not possessed of marked chemical properties. The only substances with which it is known to combine directly at ordinary temperatures, are chlorine and oxygen. Hydrogen and chlorine, mixed together, and exposed to direct sunshine, combine, with explosion. They unite gradually in diffused daylight, but do not react at all upon one another in the dark. Hydrogen and oxygen do not combine spontaneously, even in direct sunlight, but require the presence of spongy platinum *, or of a red-hot solid, or of flame.

(39) At a red heat, hydrogen has the property of abstracting oxygen or chlorine from most metallic oxides or chlorides; thus, with oxide of copper, we have $Cu_2O + H_2 = H_2O + Cu_2$; and with chloride of nickel, $NiCl + H = HCl + Ni$. Nascent hydrogen, moreover, is a powerful reducing or deoxidating agent, even at ordinary temperatures. Thus, nitric acid and nitrophenene, when acted upon by a mixture of zinc and sulphuric acid, are respectively converted into ammonia and aniline: —

$$\overbrace{HNO_3}^{\text{Nitric acid.}} + H_8 = \overbrace{H_3N}^{\text{Ammonia.}} + 3H_2O$$

$$\overbrace{C_6H_5NO_2}^{\text{Nitrophenene.}} + H_6 = \overbrace{C_6H_7N}^{\text{Aniline.}} + 2H_2O$$

(40) The double atom of hydrogen, H_2, constitutes the vanishing point of the marsh-gas series of hydrocarbons, to the members of which it closely corresponds in many of its properties, as will be hereafter shown.

Marsh-gas hydrocarbons.		Alcohols.	
C_5H_{12}	Hydride of amyl.	$C_5H_{12}O$	Amylic.
C_4H_{10}	Hydride of butyl.	$C_4H_{10}O$	Butylic.
C_3H_8	Hydride of propyl.	C_3H_8O	Propylic.
C_2H_6	Hydride of ethyl.	C_2H_6O	Ethylic.
CH_4	Hydride of methyl.	CH_4O	Methylic.
H_2	Hydrogen.	H_2O	Hydric (water).

The above table exhibits the formulæ of these hydrocarbons, and of their corresponding alcohols or oxides. Hydrogen evidently constitutes the ultimate term of this series of compounds, which,

* The action of clean platinum in causing the combination of different gases, is, with certain other phenomena, comprised under the general head of catalysis, and will be considered hereafter.

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it may be observed, are homologous, that is, differ from one another by CH_2. We have already shown how formic acid, by the loss of carbonic anhydride, yields hydrogen: $CH_2O_2 - CO_2 = H_2$. In a precisely similar manner, the homologues of formic acid yield the above hydrocarbons homologous with hydrogen; acetic acid, for instance, by the loss of carbonic anhydride, yields marsh gas or hydride of methyl: $C_2H_4O_2 - CO_2 = CH_4$.

(41) Hydrogen enters into the constitution of a great variety of compounds, acid, alkaline, and neutral, as instanced in the following examples: —

$NaHO$. . . Hydrate of sodium.	H_2SO_4 . . Sulphuric acid.
H_3N Ammonia.	HNO_3 . . . Nitric acid.
C_6H_7N . . Aniline.	$C_2H_2O_4$. . Oxalic acid.
$C_{42}H_{22}NO$ Strychnia.	$C_6H_3N_3O_7$ Picric acid.
C_2H_6O . . Alcohol.	C_2H_4 . . . Olefiant gas.
$C_{10}H_{16}O$. Camphor.	$C_{10}H_8$. . . Naphthaline.
NH_4Cl . . Sal-ammoniac.	C_8H_5NO . Indigo.

It is found that the hydrogen of these, and indeed of nearly all hydrogenised compounds, is capable of being replaced by other elements, particularly by the basylous metals, and by chlorine and its congeners. At present, we shall merely glance at the circumstances under which this replacement of hydrogen by chlorous and basylous elements can be effected, as we shall have to consider the whole subject somewhat minutely under the head of substitutions. We find in most hydrogenised bodies that some, if not all, of the hydrogen-atoms may be directly replaced by an equal number of atoms of chlorine, or bromine, or iodine; and it is observable in many cases, especially where the body is composed of several elementary atoms, that the derived or chloro-compound presents a most marked resemblance to the normal body from which it was obtained. Thus, acetic acid $C_2H_4O_2$, when submitted to the prolonged action of chlorine, is converted into trichloracetic acid $C_2HCl_3O_2$. The two acids are both crystallisable, deliquescent, soluble in water and alcohol, have the same saturating capacity, yield analogous salts, ethers, &c., and are mutually convertible by the action of nascent hydrogen and of chlorine respectively.

In most hydrogenised compounds also, it is found that the whole or a part of the hydrogen may be replaced directly or indirectly by a metal, and, as we have before observed, all these bodies must analogically be considered as acids. In ordinary language, however, we confine the term acid to such hydrogenised bodies, as when acted upon by hydrate of potassium, exchange

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hydrogen for potassium, with simultaneous formation of water, thus: —

$$H_2SO_4 + KHO = KHSO_4 + H_2O.$$

$$H_2SO_4 + 2KHO = K_2SO_4 + 2H_2O.$$

All these bodies are found to redden vegetable blues, and to effervesce with alkaline carbonates (vide par. 16).

(42) We are accustomed to classify the metals and pseudo-metals to some extent, by means of their equivalent relations with hydrogen, which constitutes, as it were, the general standard or type to which they all are referred.

a. The majority of the metals can replace hydrogen by interchange of atom for atom, so as to form proto-salts, as when chlorhydric acid HCl, becomes chloride of iron FeCl. The well known metals, lithium, sodium, potassium, calcium, strontium, barium, magnesium, zinc, and cadmium, cannot replace hydrogen in any other proportion.

β. Some few metals can replace hydrogen by an interchange of one atom of metal for two atoms of hydrogen, to form bi-salts, as when two molecules of chlorhydric acid H_2Cl_2, become one molecule of bichloride of platinum PtC_2 The tendency to this rate of replacement is manifested chiefly by palladium, platinum, titanium, and tin. The metals palladium and platinum form proto-compounds in addition, whereas titanium and tin form quadri-compounds. When the above metals replace two atoms of hydrogen, it is sometimes convenient to indicate the fact by means of two dashes placed to the right of the symbol, thus: $Pt''Cl_2$ (vide par. 11).

γ. Several metals can replace hydrogen by interchange of one atom of metal for three atoms of hydrogen, to form ter-compounds, as when three molecules of chlorhydric acid H_3Cl_3, become one molecule of ter-chloride of bismuth $BiCl_3$. These metals are principally arsenic, antimony, bismuth, molybdenum, vanadium, tungsten, and gold, which last metal only is known to form proto-compounds in addition. It is sometimes convenient to indicate this triple rate of replacement by the use of three dashes, thus: $Bi'''Cl_3$.

δ. Many metals can replace hydrogen by interchange of two atoms of metal for three atoms of hydrogen, so as to form sesqui-salts, as when three molecules of chlorhydric acid H_3Cl_3, become one molecule of sesquichloride of iron Fe_2Cl_3. The principal metals that have this property are aluminum, cerium, uranium,

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chromium, iron, manganese, nickel, and cobalt, in which last two, however, the tendency is but slight. Aluminum alone is not known to replace hydrogen in any other than the above proportion. The other metals form proto- as well as sesqui-compounds. It is sometimes convenient to represent the double atom of metal in sesqui-compounds, by doubling one of the letters of its symbol thus: All, Ffe, Mm, Uu, Ccr, &c., instead of Al_2, Fe_2, Mn_2, U_2, Cr_2, &c. The property which these double or twin atoms have of replacing three atoms of hydrogen, may then be conveniently indicated by the use of three dashes placed to the right of the symbol, thus: Ffe‴, All‴, &c.

ε. Some few metals can replace hydrogen by interchange of two atoms of metal for one atom of hydrogen to form sub- or di-salts, as when chlorhydric acid HCl, becomes sub-chloride of copper Cu_2Cl. This tendency is manifested principally by mercury and copper; also, though to an inconsiderable extent, by silver and lead. All these metals form proto-compounds in addition. It is found convenient to indicate this rate of replacement by the use of two dashes placed to the left of the symbol, thus: „Cu_2Cl. These di-equivalent metals bear to prot-equivalent metals much the same relation that sesqui-equivalent metals bear to ter-equivalent metals, and might even be represented in a similar manner by doubling one of the letters of their respective symbols. The actual or potential exchange of an atom of metal for $3\frac{1}{2}$, or 4, or 5 atoms of hydrogen occurs but very rarely.

From the above observations, it is evident that the following metals in particular have two rates of exchange for hydrogen, and we sometimes designate them by modified names, as well as by modified symbols, according to their different rates of exchange, thus: —

„Cu Cuprosum.	Cu′ Cupricum.
„Hg Mercurosum.	Hg′ Mercuricum.
Pt′ Platinosum.	Pt″ Platinicum.
Au′ Aurosum.	Au‴ Auricum.
Cr′ Chromosum.	Ccr‴ Chromicum.
Fe′ Ferrosum.	Ffe‴ Ferricum.
Mn′ Manganosum.	Mm‴ Manganicum.
U′ Uranosum.	Uu‴ Uranicum.
Sn″ Stannosum.	Sn⁗ Stannicum.
	As‴ Arsenicum.
	Sb‴ Antimonicum.
	Bi‴ Bismuthicum.
	All‴ Aluminicum.

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The metals arsenic, antimony, bismuth, and aluminum, have received the above names in anticipation of the discovery of their proto-compounds. In speaking of metallic salts, we employ the terminations, *ous* and *ic*, to indicate the replaceable value of the metal; thus, we have mercurous and mercuric, platinous and platinic, ferrous and ferric salts, &c.

(43) From the many analogies of hydrogen to a metal, from the facility with which hydrogen may be replaced by a metal, and from the circumstance that hydrogen gas differs in no important physical property from mercurial vapour, Dumas has speculated, that if we could succeed in reducing hydrogen gas to the liquid state, as we can reduce mercurial vapour, the liquid hydrogen, like the liquid mercury, would assume a metallic aspect. But it must be remembered, that hydrogen has a chlorous as well as a basylous face, and that its chlorous analogies are as decided, as important, and as frequent as are its basylous relations. Hydrogen is essentially a neutral or intermediate body, and judging from its relations with homologous condensible hydrocarbons, and from its chlorous habitudes, we should not, I think, expect to find liquid hydrogen possess the appearance of a metal.

(44) In addition to the above described elementary substitutions of metals and halogens for hydrogen, we find that certain molecular groupings, usually known as compound radicles, can also be transferred with great facility, from one compound to another, in exchange for one or more atoms of hydrogen or of its representatives, thus: —

Chloride of benzoyl. Benzamide.

$$\overbrace{(C_7H_5O)Cl} + NH_3 = HCl + \overbrace{NH_2\,(C_7H_5O)}$$

Similarly, in chloride of ethylene $(C_2H_4)''Cl_2$, we have a bi-equivalent radical, and in chloride of phosphoryl $(PO)'''Cl_3$, a ter-equivalent radical, which can replace two and three atoms of hydrogen respectively, like the mult-equivalent metals (vide paragraphs 23, 24, 25)

(45) *Summary.* — Combined hydrogen in the state of water has an extensive natural distribution. Free hydrogen is prepared by various processes, usually by the action of an easily oxidisable metal upon an acid, or body playing the part of an acid. It is a permanent, very light, inflammable gas, and when mixed with oxygen or chlorine, explosive. It unites with chlorine to form chlorhydric acid, with oxygen to form water, with nitrogen to form ammonia, and enters into the composition of numerous other and

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very varied compounds. At a red heat, or in the nascent state, it is a powerful deoxidating and dechlorinating agent. It is the vanishing term of a series of homologous hydrocarbons. It is essential to the constitution of an acid. It can be replaced by chlorine and its congeners, by the metals, and by certain molecular groupings. One atom of a metal may replace one atom, or half an atom, or several atoms of hydrogen.

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CHAPTER II.

(46) Elements which unite with hydrogen in the proportion of atom to atom, gaseous atomic volume to gaseous atomic volume, namely, fluorine, chlorine, bromine, and iodine. The members of this group of elements constitute the halogens.

§ I. Chlorine.

Symbol Cl; *Proportional number* 35·5; *Density* 35·5; *Atomic volume* □.

(47) Chlorine is a substance very widely distributed in nature. It exists chiefly in the form of chloride of sodium, which constitutes rock-salt when deposited in inland beds, sea-salt when dissolved in masses of water. The sea also contains chlorides of potassium, calcium, and magnesium. The chlorides of calcium, lead, mercury, and silver, respectively, form the partial or sole constituents of several well known minerals, and free chlorhydric acid has been met with in the air of volcanic neighbourhoods. Chlorine was discovered by Scheele in 1774. Its elementary nature was first established by Davy in 1810.

(48) *a.* Chlorine is usually prepared by the action of chlorhydric acid upon peroxide of manganese, at a gentle heat: —

$$4HCl + Mn_2O_2 = 2H_2O + 2MnCl + Cl_2.$$

The liberated chlorine may be washed by transmission through a small quantity of water, and dried with oil of vitriol in the usual manner. It is best collected by downward displacement. It cannot be collected over mercury, on account of its rapid action on the metal. It cannot readily be collected over water, on account of solubility therein; but the difficulty may be obviated by evolving the gas rapidly, or by passing the delivery tube to the summit of the receiver, or by keeping the water in the trough perceptibly warm, or by saturating it with common salt. In the above reaction, the peroxide of manganese may be replaced by bichromate of potassium; as also, though with questionable advantage, by several other oxidising agents, such as red or brown oxide of lead, chlorate of potassium, hypochlorite of calcium, nitric acid, &c. Moreover, a mixture of common salt and oil of vitriol, which generates chlorhydric acid abundantly,

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may be, and frequently is, substituted for the ready formed chlorhydric acid, thus: —

$$2NaCl + 2H_2SO_4 + Mn_2O_2 = Na_2SO_4 + Mn_2SO_4 + 2H_2O + Cl_2$$

β. Chlorine is also liberated by the simple action of a red heat upon certain chlorides, such as those of palladium, platinum, and gold, thus: $PtCl_2 = Pt + Cl_2$. Pentachloride of antimony $SbCl_5$ breaks up, when gently heated, into terchloride of antimony $SbCl_3$, and free chlorine Cl_2; and in a similar manner, the terchloride of gold $AuCl_3$, breaks up into protochloride of gold AuCl, and free chlorine Cl_2. Moreover, chlorine gas frequently results from the decomposition of its oxidised compounds.

(49) Chlorine has a yellowish green colour, whence its name (*χλωρος*), and a pungent irritating smell. It is irrespirable unless very much diluted. It is one of the heaviest substances that are gaseous at common temperatures, being $35\frac{1}{2}$ times heavier than hydrogen, and $2\frac{1}{2}$ times heavier than atmospheric air. By a pressure of four atmospheres, at mean temperature 15·5°, it is condensed into a yellow mobile liquid, having a specific gravity 1·33. It has resisted all attempts at solidification. At ordinary temperatures, water dissolves about twice its volume of chlorine, forming a solution which has the colour, smell, and general chemical properties of the gas. At lower temperatures, water dissolves a still greater proportion of chlorine, and at the temperature 0° a definite hydrate of chlorine $Cl. 5H_2O$ crystallises out. If this hydrate be gently warmed in a sealed tube, it will, at a temperature of 38°, decompose into a layer of water floating over a layer of liquid chlorine. This liquid chlorine may be readily distilled off, and condensed by means of a freezing mixture at the other extremity of the tube, which is usually bent for this purpose at an obtuse angle. Unlike hydrogen, chlorine is a body which possesses very active chemical properties, and gives origin to many phenomena of combination, substitution, and indirect oxidation. It is, moreover, non-inflammable, and does not unite directly with oxygen under any circumstances. At ordinary temperatures, chlorine combines directly with all the metals, with many non-metals, such as hydrogen and phosphorus, and with many compound bodies, such as sulphurous anhydride SO_2, olefiant gas C_2H_4, phenene C_6H_6, and carbonic oxide CO. Its union with phosphorus, and with finely divided arsenic, antimony, tin, or copper, is attended with the phenomena of combustion. At increased temperatures, chlorine combines with many other substances, such as sulphur, selenium, boron, and silicon.

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It has not been made to combine directly with carbon. When ordinary combustible bodies containing carbon and hydrogen, such as paper, wood, wax-taper, &c., are ignited and immersed in a vessel of chlorine, the combustion continues chiefly at the expense of the hydrogen, which forms chlorhydric acid, while the carbon is deposited as a dense black smoke. Previous ignition of the hydrocarbonised substance is not always necessary to induce these phenomena. Paper dipped in oil of turpentine C_8H_{20}, and plunged in a vessel of the gas, takes fire spontaneously, yielding abundance of chlorhydric acid and carbon.

(50) Chlorine has the property of displacing bromine and iodine from their combinations, by equivalent substitution. Free iodine strikes a deep blue colour with starch; and when starched paper dipped in iodide of potassium solution is brought into contact with chlorine, the iodine is liberated by the chlorine, and the characteristic blue iodide of starch produced: $KI + Cl = KCl + I$. Chlorine also displaces hydrogen by equivalent substitution; one half of the chlorine takes the place of an equivalent quantity of hydrogen, while the other half unites with the hydrogen eliminated:—

$$\overbrace{C_{13}H_{18}O_7}^{\text{Salicin.}} + Cl_2 = \overbrace{C_{13}H_{17}ClO_7}^{\text{Chlorosalicin.}} + HCl.$$

$$\overbrace{C_2H_4O_2}^{\text{Acetic acid.}} + Cl_6 = \overbrace{C_2HCl_3O_2}^{\text{Trichloracetic acid.}} + 3HCl.$$

Chlorine, by combining with hydrogen or a metal, acts indirectly as an oxidising agent. Thus, when chlorine-water is exposed to the action of sunlight, we have $Cl_2 + H_2O = 2HCl + O$. Again, when ferric hydrate, suspended in solution of hydrate of potassium, is treated with chlorine, we have produced ferric and chlorhydric acids, which react with the alkali to form potassium salts: —

$$H_2O + \overbrace{Fe_2H_3O_3}^{\text{Ferric hydrate.}} + Cl_3 = H_2O \,.\, Fe_2O_3 \quad (i.e.\ \overbrace{H_2Fe_2O_4}^{\text{Ferric acid.}}) + 3HCl.$$

Chlorine destroys the colour of most organic pigments. This bleaching action is usually accompanied both by oxidation and substitution, thus: —

$$\overbrace{C_8H_5NO}^{\text{Indigo.}} + H_2O + Cl_4 = \overbrace{C_8H_4ClNO_2}^{\text{Chlorisatin.}} + 3HCl.$$

Chlorine also destroys odours of various kinds, and possibly infectious miasmata, either by abstracting hydrogen with or without substitution, or by indirectly oxidising.

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Chlorhydric Acid.

Symbol HCl; *Proportional number* 36·5; *Density* 18·25; *Atomic volume* □□.

(51) Chlorhydric acid gas is the only known compound of chlorine and hydrogen. Its solution in water has been made use of from a very early period, and has received successively the names, spirit of salt, muriatic acid, hydrochloric acid, and lastly, chlorhydric acid. Chlorhydric acid gas was discovered by Priestley in 1772.

(52) *a.* Chlorhydric acid is usually prepared by the action of strong sulphuric acid upon fused common salt. There is, at first, a copious effervescence, which, after some time, it may be necessary to revive by the application of a gentle heat. The gas must be collected over the mercurial trough, on account of its great solubility in water :—

$$H_2SO_4 + NaCl = \overbrace{NaHSO_4}^{\text{Acid sulph. sodium.}} + HCl.$$

β. Chlorhydric acid may also be prepared by the direct union of its constituent elements. Two bottles of exactly equal capacity and fitted to one another by grinding, are filled by displacement with dry hydrogen and dry chlorine respectively. The bottles are then adapted to one another by their mouths, that with the chlorine being placed uppermost, and the two set aside for some hours in a light situation, but excluded from the direct rays of the sun. Combination takes place gradually, and after the greenish colour of the chlorine has almost disappeared, a few minutes' exposure to direct sunlight will determine the entire reaction. The two bottles may then be separated from one another under mercury, when each will be found full of chlorhydric gas. No gas will escape from either bottle through an increased pressure or expansion, nor will any mercury rise in either bottle through a decreased pressure or contraction, of the contained chlorhydric acid. In other words, the resulting compound gas has exactly the same volume and tension as had the two constituent gases prior to their union. If a jet of water tinged with blue litmus be thrown up into one of the bottles, the gas will be readily and completely absorbed, the mercury rising to supply its place, while the litmus solution will assume a bright red colour. Any bleaching of the litmus would indicate the presence of free chlorine; any unabsorbed gas, the presence of free hydrogen, which latter might be transferred and inflamed. If, in

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performing the above experiment, any excess of chlorine or hydrogen be employed, the excess will remain unacted upon, and may be detected as above described.

γ. Chlorhydric acid may also be produced by the action of water on certain chlorides. The two chlorides of phosphorus are decomposed immediately and completely by mixture with an excess of water, thus: —

Terchloride phosphorus. Phosphorous acid.

$$\overbrace{PCl_3} + 3H_2O = \overbrace{H_3PO_3} + 3HCl.$$

Pentachloride phosphorus. Phosphoric acid.

$$\overbrace{PCl_5} + 4H_2O = \overbrace{H_3PO_4} + 5HCl.$$

The two chlorides of antimony are decomposed more slowly. Terchloride of bismuth requires prolonged treatment with water to effect its thorough decomposition, which, however, takes place readily at a boiling temperature. Stannic chloride, even at a boiling temperature, is decomposed very imperfectly. The sesquichloride of aluminum and protochloride of magnesium, &c., are decomposed by steam with evolution of chlorhydric acid, at temperatures considerably below redness: —

$$2Al_2Cl_3 + 3H_2O = Al_4O_3 + 6HCl.$$

$$2MgCl + H_2O = Mg_2O + 2HCl.$$

Moreover, chlorhydric acid results from the reaction of chloride of phosphorus, chloride of antimony, and some other chlorides, usually hyperchlorides, not only with water, but with most oxyhydrogenised compounds.

δ. We have seen that chlorhydric acid is a constant attendant upon the direct action of chlorine on hydrogenised substances. The reaction of chlorine upon sulphydric acid is interesting, as typical of the mode in which bromhydric and iodhydric acids are usually formed, thus: $H_2S + Cl_2 = 2HCl + S$. This reaction is obviously analogous to the spontaneous decomposition of chlorine-water, already adverted to. Chlorhydric acid also results from the inverse action of hydrogen upon a chlorine compound, as when ignited chloride of nickel is subjected to a current of hydrogen, thus: $NiCl + H = HCl + Ni$.

(53) Chlorhydric acid is a colourless gas, having a strong acid taste, and a pungent irritating odour. It forms opaque white fumes in the air, owing to its union with, and condensation of, the atmospheric moisture. In perfectly dry air these fumes are not produced. The gas is extremely soluble in water. When a flask of dry chlorhydric acid is opened under water, the whole of the gas is ab-

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sorbed in an instant, and the flask not unfrequently broken by the violent rush of liquid. At mean temperature 15°, water dissolves about 480 times its volume of the gas. At the temperature of 10°, under a pressure of 40 atmospheres, chlorhydric acid is condensed into a colourless liquid, having a specific gravity 1·27. It has never been solidified. Chlorhydric acid is not inflammable, and extinguishes most burning bodies, but when a piece of potassium is introduced by means of an iron wire into a tube full of the gas retained over mercury, and is then heated to redness by a spirit lamp applied externally, it undergoes combustion, unites with the chlorine, and leaves the hydrogen, which is eventually found to occupy exactly one half the volume of the original gas: $HCl + K = KCl + H$.

(54) Solution of chlorhydric acid is usually made from common salt and sulphuric acid diluted with about two-thirds its bulk of water. The reaction is effected in a retort to which a gentle heat is applied, and the evolved gas is condensed in a vessel or series of vessels of distilled water. The condensing liquid increases considerably in bulk, and may eventually be made to acquire a specific gravity of 1·21, under which circumstances it consists of one atom of chlorhydric acid HCl, dissolved in three atoms of water H_2O. Solution of chlorhydric acid has usually a specific gravity of 1·162, and then consists of one atom of chlorhydric acid HCl, dissolved in four atoms of water H_2O. Commercial muriatic acid is made by heating in iron cylinders two proportions of common salt, with as much brown sulphuric acid as contains one proportion of real acid, and condensing the evolved gas in water contained in a series of stoneware Wolfe's bottles. The reaction is,

$$H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl.$$

The commercial acid, which frequently contains, as impurities, sulphurous acid, arsenious acid, sesquichloride of iron, stannic chloride, and even free chlorine, may be partly purified by dilution and redistillation. A pure solution of chlorhydric acid is usually colourless, but when in large quantities, has a very pale yellowish green tint. The slight yellow colour of miscalled pure acid is generally due to the presence of free chlorine or of organic matter, but the bright deep yellow of the commercial acid results from the presence of chloride of iron. A strong solution of chlorhydric acid evolves fumes on exposure to air. When boiled it gives off chlorhydric acid gas, until the temperature slightly exceeds 100°, when there distils over a diluted solution of the acid, having a specific gravity of 1·1, and consisting of one atom of chlorhydric acid HCl, dissolved in

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eight atoms of water H_2O. The solutions of chlorhydric gas have powerful acid properties, redden litmus, taste intensely sour, effervesce with carbonates, and dissolve many metals with evolution of hydrogen. They do not bleach vegetable colours, or dissolve gold leaf.

Chlorhydric acid is typical of many other compounds, to be hereafter described. Thus, we have the fluorhydric, bromhydric, and iodhydric acids, in which the chlorine of chlorhydric acid is replaced by some other chlorous element, and the large class of metallic chlorides, in which the hydrogen of chlorhydric acid is replaced by some more or less basylous element.

Chlorides.

(55) These compounds may be looked upon as derivatives of one or more atoms of chlorhydric acid, by the substitution of metal or quasi-metal for hydrogen. They may be arranged in the following principal groups: —

a. Chlorides with one atom of chlorine, formed on the type of the single atom of chlorhydric acid, HCl, namely, protochlorides, and di- or subchlorides.—All those metals that are prot-equivalent, or capable of replacing hydrogen by interchange of atom for atom, of which the principal are lithium, sodium, potassium, calcium, strontium, barium, magnesium, zinc, cadmium, chromium, manganese, iron, nickel, cobalt, copper, mercury, lead, silver, palladium, platinum, and gold, form protochlorides; for example, protochloride of barium BaCl, protochloride of copper CuCl, &c. In these chlorides, the prefix proto- is, for the sake of brevity, generally omitted, save when the metal forms some other chloride in addition, as is the case with copper and mercury, which form subchlorides; with chromium, manganese and iron, which form sesquichlorides; with palladium and platinum, which form bichlorides; and with gold, which forms a terchloride. The protochlorides of platinum and silver are quite insoluble in water, hot or cold, but all other protochlorides are more or less soluble. The protochlorides of gold, platinum, and palladium, are completely decomposed at a red heat, and that of copper is partially decomposed. The remaining chlorides fuse when heated, and at an increased temperature volatilise unchanged. Several hydrated protochlorides, those of magnesium and zinc for instance, are decomposed more or less completely by heat, into metallic oxide and chlorhydric acid. The fused protochlorides are electrolytic.

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The di-equivalent metals, copper and mercury especially, furnish subchlorides, compounds in which the single hydrogen-atom of chlorhydric acid is replaced by a double atom of metal, thus: HCl, Cu_2Cl, Hg_2Cl. The subchlorides are all insoluble in water, and, under certain circumstances, manifest a tendency to decompose into metal and protochloride.

β. Chlorides with two atoms of chlorine, formed on the type of the double atom of chlorhydric acid, H_2Cl_2, namely, bichlorides.— These chlorides, as shown in the accompanying table, are derived from two molecules of chlorhydric acid, by the substitution of one atom of a bi-equivalent metal for the two atoms of hydrogen: —

H_2 Cl_2	Chlorhydric acid.
Te″ Cl_2	Bichloride of tellurium.
Sn″ Cl_2	Bichloride of tin (stannous chloride).
Ti″ Cl_2	Bichloride of titanium (titanous chloride).
Mo″ Cl_2	Bichloride of molybdenum.
V″ Cl_2	Bichloride of vanadium.
W″ Cl_2	Bichloride of tungsten.
Pd″ Cl_2	Bichloride of palladium.
Pt″ Cl_2	Bichloride of platinum.

The bichlorides of platinum and palladium give off at a gentle heat one half, and at a stronger heat the whole of their chlorine. The remaining bichlorides are readily volatile, and manifest a general resemblance in their other properties.

γ. Chlorides with three atoms of chlorine, formed on the type of the treble atom of chlorhydric acid, H_3Cl_3, namely, terchlorides and sesquichlorides. — The terchlorides, as shown in the accompanying table, are derived from three molecules of chlorhydric acid, by the substitution of one atom of a ter-equivalent metal, or quasi-metal, for the three atoms of hydrogen: —

H_3 Cl_3	Chlorhydric acid.
P‴ Cl_3	Terchloride of phosphorus.
As‴ Cl_3	Terchloride of arsenic.
Sb‴ Cl_3	Terchloride of antimony.
Bi‴ Cl_3	Terchloride of bismuth.
Mo‴ Cl_3	Terchloride of molybdenum.
V‴ Cl_3	Terchloride of vanadium.
W‴ Cl_3	Terchloride of tungsten.
Au‴ Cl_3	Terchloride of gold.

The terchloride of gold, like the bichlorides of platinum and palladium, is converted at a gentle heat into protochloride, which a stronger heat completely decomposes. The other terchlorides

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volatilise unchanged. Those of antimony and bismuth are very fusible solids, the remainder are liquids. The volatile terchlorides are obviously decomposed by water, and correspond closely with one another in most of their properties.

The sesquichlorides, as shown in the accompanying table, are formed from three molecules of chlorhydric acid, by the substitution of two atoms of a sesqui-equivalent metal for three atoms of hydrogen, thus: —

		H_3 Cl_3	Chlorhydric acid.
Al_2Cl_3	or	All‴ Cl_3	Sesquichloride of aluminum.
Ce_2Cl_3	or	Cee‴ Cl_3	Sesquichloride of cerium.
Cr_2Cl_3	or	Ccr‴ Cl_3	Sesquichloride of chromium.
Fe_2Cl_3	or	Ffe‴ Cl_3	Sesquichloride of iron.
Mn_2Cl_3	or	Mm‴ Cl_3	Sesquichloride of manganese.

The sesquichlorides of cerium and manganese are known only in the hydrated state. The other three sesquichlorides are fusible volatile solids. All the hydrated sesquichlorides are partially decomposed when heated.

δ. *Chlorides with four atoms of chlorine, formed on the type of the quadruple atom of chlorhydric acid,* H_4Cl_4, *namely, tetrachlorides.* — The following are examples, C⁗Cl_4 tetrachloride of carbon, Si⁗Cl_4 tetrachloride of silicon, Ti⁗Cl_4 tetrachloride of titanium, Sn⁗Cl_4 tetrachloride of tin.* The tetrachlorides exist ordinarily in the liquid state. They are all volatile, and their respective vapour-densities are the halves of their atomic weights, or, in other words, their molecules correspond to the normal two-volume standard. Each tetrachloride has a corresponding bichloride, and the general behaviour of the tetrachlorides shows that two of the chlorine atoms are held less forcibly than are the other two.

ε. *Chlorides with five atoms of chlorine, formed on the type of five atoms of chlorhydric acid,* H_5Cl_5, *namely pentachlorides.* The following are examples: — PCl_5 pentachloride of phosphorus, $SbCl_5$ pentachloride of antimony. These pentachlorides are both volatile, but that of antimony undergoes partial decomposition. To each pentachloride there is a corresponding terchloride, and the general relations of the pentachlorides indicate that two of the chlorine atoms are retained less forcibly than are the other two. The pentachlorides are completely decomposed by excess of water. With an insufficient amount of water, they produce oxichlorides,

* All these tetrachlorides were formerly known as bichlorides.

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or chloraldehyds, compounds in which two atoms of chlorine are exchanged for one of oxygen, thus: $PCl_5 + H_2O = PCl_3O + 2HCl$.

There are no hexachlorides known, and only one heptachloride, namely, the heptachloride of manganese Mn_2Cl_7.

(56) The chlorides are generally prepared by one or other of the following processes. *α.* By acting upon the metal with chlorine gas. This method is frequently employed for the preparation of anhydrous chlorides. The pentachloride of antimony and protochloride of copper are examples of chlorides sometimes produced in this manner. The chlorides of gold and platinum are usually prepared by acting upon the metals with nascent chlorine, developed by the mutual reaction of chlorhydric and nitric acids. Sometimes, on the other hand, the metal is in a nascent state, as when titanic chloride is formed by passing a current of chlorine over a heated mixture of charcoal and titanic anhydride.

β. Chlorine gas, by its action upon metallic oxides, drives out the oxygen, and unites with the respective metals to form chlorides. This reaction sometimes takes place at ordinary temperatures, as is the case with oxide of silver; sometimes only at a red heat, as is the case with the oxides of the alkali- and alkaline earth metals. The hydrates and carbonates of these last metals, when dissolved or suspended in hot water and treated with excess of chlorine, are converted, chiefly into chlorides, partly into chlorates.

γ. Many chlorides are prepared by acting upon the metals with chlorhydric acid. Zinc, cadmium, iron, nickel, cobalt, and tin, dissolve readily in chlorhydric acid, with liberation of hydrogen; copper only in the strong boiling acid; silver, mercury, palladium, platinum, and gold, not at all. Sometimes the metal is substituted, not for hydrogen, but for some other metal. Stannous chloride, for instance, is frequently made by distilling metallic tin with mercuric chloride, thus: $2HgCl + Sn = SnCl_2 + Hg_2$.

δ. Or we may dissolve the oxide, hydrate, or carbonate of metal in chlorhydric acid. In this way the hydrated protochloride of copper, and sesquichloride of iron are usually made:—

$$Cu_2O + 2HCl = H_2O + 2CuCl.$$
$$Fe_2H_3O_3 + 3HCl = 3H_2O + Fe_2Cl_3.$$

With a peroxide, the reaction is accompanied by an evolution of chlorine, as we have already seen, thus:—

$$Pb_2O_2 + 4HCl = 2H_2O + 2PbCl + Cl_2$$

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Chlorhydric acid, and all metallic chlorides, when heated with sulphuric acid and a peroxide, give off free chlorine, easily recognised by its colour, smell, bleaching properties, and reaction with starch and iodide of potassium.

ε. Owing to their insolubility, the chlorides of silver and lead and the subchloride of mercury are readily prepared by precipitating any of their corresponding soluble salts, with chlorhydric acid or a soluble chloride, thus: —

$$NaCl + Hg_2NO_3 = Hg_2Cl + NaNO_3.$$
$$FeCl + AgNO_3 = AgCl + FeNO_3.$$
$$Fe_2Cl_3 + 3AgNO_3 = 3AgCl + Fe_2(NO_3)_3.$$

Free chlorine, chlorhydric acid, and all soluble metallic chlorides, give with solution of nitrate of silver a white precipitate of chloride of silver, recognisable by its solubility in ammonia, and its insolubility in boiling nitric acid. A moiety only of the free chlorine present in a liquid is at once precipitated by solution of nitrate of silver, the other half being converted by the precipitation into hypochlorous acid.

All metallic chlorides, excepting those of the alkali- and earth-metals, are decomposed at a red heat by hydrogen gas, with formation of chlorhydric acid. In this way metallic iron may be produced in fine cubical crystals, thus: $FeCl + H = HCl + Fe$. Several metallic chlorides are decomposed by oxygen gas at a red heat. The chlorides of the basylous metals and of hydrogen frequently unite with the chlorides of the less basylous metals, to form well-defined crystallisable double salts, as instanced by the double chloride of potassium and mercury KCl . HgCl.

Oxidised Compounds of Chlorine.

(57) The acids and potassium salts of chlorine are the following: —

Chlorhydric acid	HCl	.	KCl	Chloride.
Hypochlorous acid	$HClO$	.	$KClO$	Hypochlorite.
Chlorous acid	$HClO_2$	.	$KClO_2$	Chlorite.
Chloric acid	$HClO_3$	.	$KClO_3$	Chlorate.
Perchloric acid	$HClO_4$	.	$KClO_4$	Perchlorate.

The potassium salts may all be made from their corresponding acids by the action of hydrate of potassium; and the acids may all be made from their corresponding potassium salts by the action of

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sulphuric, or of fluosilicic acid. The respective acids, or their salts, are convertible into one another by the following processes: —

α. Hypochlorous acid $HClO$, may be made by oxidising chlorhydric acid HCl, with permanganic acid; and conversely by deoxidating hypochlorous acid with sulphite of sodium, the chlorhydric acid may be reproduced.

β. Solution of hypochlorous acid $HClO$, especially at increased temperatures, is converted spontaneously into chloric acid $HClO_3$, together with water, chlorine, and oxygen. Moreover the solution of an alkaline hypochlorite, when boiled for some time, breaks up into chlorate and chloride: $3KClO = KClO_3 + 2KCl$.

γ. Chloric acid $HClO_3$, when deoxidated by nitrous acid, yields chlorous acid $HClO_2$; and conversely chlorous acid by its spontaneous decomposition yields chloric acid and other products.

δ. Chloric acid $HClO_3$, when oxidated at the positive pole of a voltaic battery becomes perchloric acid $HClO_4$. Moreover chlorate of potassium, when moderately heated, breaks up into perchlorate of potassium, chloride of potassium, and oxygen.

Hypochlorites, chlorites, chlorates, and perchlorates of alkali-metal, when strongly heated, are alike converted into chlorides by loss of oxygen.

The anhydride of a monobasic oxygen-acid is formed from two atoms of the acid by the loss of one atom of water, as we have already seen (vide par. 21). The chlorine-acids should therefore yield the following anhydrides: —

Acids.				Anhydrides.	
$2HClO$	$-$	H_2O	$=$	Cl_2O	Hypochlorous.
$2HClO_2$	$-$	H_2O	$=$	Cl_2O_3	Chlorous.
$2HClO_3$	$-$	H_2O	$=$	Cl_2O_5	Chloric.
$2HClO_4$	$-$	H_2O	$=$	Cl_2O_7	Perchloric.

The first two anhydrides are tolerably well known, the last two have not yet been obtained. We are, however, acquainted with the corresponding iodic and periodic anhydrides, I_2O_5 and I_2O_7 respectively. By the reabsorption of an atom of water, one atom of each anhydride is reconverted into two atoms of the corresponding acid: —

	Cl_2O	$+$ H_2O	$=$	$2HClO$.	
	Cl_2O_3	$+$ H_2O	$=$	$2HClO_2$.	
(I_2O_5 or)	Cl_2O_5	$+$ H_2O	$=$	$2HClO_3$	(or $2HIO_3$).
(I_2O_7 or)	Cl_2O_7	$+$ H_2O	$=$	$2HClO_4$	(or $2HIO_4$).

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In addition to the above anhydrides, a complete series of chlorine-oxides should obviously include three other terms, thus:—

Cl_2	Chlorine.
Cl_2O	Hypochlorous anhydride.
Cl_2O_2	Chloric oxide. ?
Cl_2O_3	Chlorous anhydride.
Cl_2O_4	Perchloric oxide.
Cl_2O_5	Chloric anhydride.
Cl_2O_6	Hyperchloric oxide. ?
Cl_2O_7	Perchloric anhydride.

Soubeiran obtained from euchlorine, a gas which decomposed into equal volumes of chlorine and oxygen, a result considered by Berzelius to be conclusive of the existence of chloric oxide. Hyperchloric oxide is not improbably identical with Millon's perchloro-chloric acid Cl_6O_{17}, or $3Cl_2O_6$? Perchloric oxide is a very well-known substance, which, moreover, appears to be identical with Millon's chloro-chloric acid Cl_6O_{13}, or $3Cl_2O_4$? Perchloric oxide is decomposed by water into chlorous and chloric acids:—

$$Cl_2O_4 + H_2O = HClO_2 + HClO_3.$$

Hypochlorous Anhydride, Acid, and Salts.

(58) Hypochlorous anhydride. *Sym.* Cl_2O; *p.n.*87; *v.d.*43·5; □□.—*a.* This gas may be prepared by adding glacial phosphoric acid to a concentrated solution of hypochlorous acid, standing over mercury. The glacial phosphoric acid abstracts water from the hypochlorous acid, and the gaseous anhydride thus produced collects in the upper part of the tube:—

$$2HClO - H_2O = Cl_2O.$$

β. This anhydride may also be prepared by passing chlorine gas over mercuric oxide contained in a tube kept cool by ice:—

$$Hg_2O + Cl_4 = Cl_2O + 2HgCl.$$

The mercuric oxide should be prepared by precipitation, and dried at a somewhat high temperature, 300°. Any excess of mercuric oxide remains combined with the resulting mercuric chloride in the form of a brown crystalline oxichloride. The gas may be collected by downward displacement, or in the mercurial trough, but it cannot be kept long over mercury, as it gradually acts upon the metal.

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Hypochlorous anhydride is a gas of a pale reddish yellow colour, and a powerful odour somewhat resembling that of chlorine. It is so readily decomposed, into two volumes of chlorine and one volume of oxygen, that it cannot be preserved unchanged, even for a few hours. By a slight elevation of temperature, or sometimes spontaneously, decomposition takes place with explosion. In sunlight the decomposition is very rapid, but usually tranquil. At the low temperature produced by a mixture of salt and ice, the gas is condensed into a deep orange-coloured liquid, heavier than water, and very explosive. Both the gaseous and liquid anhydride dissolve in water, undergoing decomposition and being converted into hypochlorous acid: —

$$Cl_2O + H_2O = 2HClO.$$

The general reactions of the anhydride correspond with those of the acid, but are more violent.

(59) HYPOCHLOROUS ACID. *Sym.* HClO; *p.n.*52·5. — This acid may be prepared,

a. From the anhydride, as we have just seen.

β By passing air saturated with chlorhydric acid through a solution of permanganate of potassium, acidulated with sulphuric acid, and heated in a water bath. The distillate is a solution of hypochlorous acid formed by the direct oxidation of chlorhydric acid:—

$$HCl + O = HClO.$$

γ. By the addition of almost any oxacid to a metallic hypochlorite.

δ. By passing chlorine gas into water, holding suspended or dissolved certain metallic oxides, hydrates, carbonates, sulphates, phosphates, &c. In practice, oxide of mercury and, according to Williamson, carbonate of calcium, are found to be the most advantageous. Either of these substances is to be agitated with water, and treated with chlorine gas: —

$$Ca_2CO_3 + H_2O + Cl_4 = CO_2 + 2HClO + 2CaCl.$$

The product of the action is to be distilled off, and if necessary concentrated by one or two redistillations of the most volatile distillates.

Aqueous hypochlorous acid has a yellowish colour, an acrid taste, and a characteristic sweet chloroïd smell. The strong acid decomposes rapidly, even when kept in ice. The dilute acid is more stable, but is decomposed by long boiling into chloric acid,

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water, chlorine, and oxygen. Hypochlorous acid, like chlorine, possesses powerful bleaching properties. Moreover, chloro-derivatives may be produced by its agency, thus: —

Phenene. Chlorophenene.

$$\overbrace{C_6H_6} + HClO = \overbrace{C_6H_5Cl} + H_2O.$$

Chlorhydric acid decomposes hypochlorous acid, with formation of chlorine: —

$$HClO + HCl = H_2O + Cl_2.$$

Hypochlorous acid is a very powerful oxidising agent. It rapidly converts many of the elements, iodine, selenium, and arsenic, for instance, into their highest oxides, at the same time liberating chlorine. The metals differ much from one another in the nature of their respective reactions with hypochlorous acid. Those which decompose the acid form oxides, as does iron, or oxichlorides, as do copper and mercury. Silver, indeed, forms a chloride and liberates oxygen, thus: —

$$Ag_2 + 2HClO = 2AgCl + H_2O + O.$$

Many metallic oxides, those of manganese, cobalt, and lead, for example, are peroxidised with liberation of chlorine; but oxide of silver is converted into chloride of silver, with liberation of oxygen: —

$$Ag_2O + 2HClO = 2AgCl + H_2O + O_2.$$

(60) HYPOCHLORITES. — *a*. Pure hypochlorites are made by neutralising hypochlorous acid with hydrates, such for instance as those of sodium, potassium, calcium, barium, magnesium, zinc, copper, &c. — *β*. Hypochlorites are usually prepared by passing chlorine gas into solutions of hydrated or carbonated alkali, or over the dry hydrates of the earths. By this process a chloride and a hypochlorite are simultaneously produced. The reaction is believed to be as follows: —

$$Cl_2 + 2CaHO = CaCl + CaClO + H_2O.$$

These mixed compounds constitute the bleaching salts of commerce, and are generally known by the unsystematic names, chloride of lime, chloride of soda, &c.

The great mass of evidence, founded partly on the similar characters of the mixed and of the pure salts, and partly on the analogy of the reaction to others of a similar nature, which are indisputable, such as that of chlorine upon carbonate of calcium,

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is favourable to the above view, which makes ordinary bleaching powder contain preformed chloride of calcium. But it is found that alcohol does not extract chloride of calcium from bleaching powder, as we should *à priori* expect; and, unlike mixtures containing chloride of calcium, bleaching powder is not deliquescent. These anomalies may possibly be due to the formation of a double salt, containing chloride and hypochlorite of calcium in chemical combination with one another.

The pure hypochlorites, when acted upon by sulphuric acid, or even by carbonic acid, liberate hypochlorous acid, thus: —

$$2CaClO + H_2SO_4 = 2HClO + Ca_2SO_4.$$

The mixed salts behave in the same manner, provided the sulphuric acid be not in excess; but otherwise chlorine, and not hypochlorous acid, is evolved: —

$$CaClO + CaCl + H_2SO_4 = H_2O + Cl_2 + Ca_2SO_4.$$

The sulphuric acid acts first upon the hypochlorite to liberate hypochlorous acid, and then upon the chloride to liberate chlorhydric acid, the co-existence of which two acids cannot occur, owing to their mutual decomposition into water and free chlorine, as we have already seen. Chlorhydric acid can liberate hypochlorous acid from the pure or mixed salts, thus: $NaClO + HCl = HClO + NaCl$. But any excess of chlorhydric acid immediately reacts upon the nascent hypochlorous acid to form water and chlorine. Solutions of the hypochlorites, pure or commercial, are very unstable, but are more permanent in the presence of free alkali. They gradually give off oxygen gas, and finally yield mixtures of chloride and chlorate. Their decomposition takes place very definitely at a boiling temperature, thus: —

$$3CaClO = CaClO_3 + 2CaCl.$$

Of themselves they act as bleaching agents, probably by evolution of oxygen; but the effects produced by acidifying their solutions, and thereby liberating hypochlorous acid, are much more rapid. With most metallic oxides and salts, the hypochlorites react as does hypochlorous acid upon the oxides. They convert oxide of silver, for instance, into chloride of silver, with liberation of oxygen: —

$$Ag_2O + 2NaClO + H_2O = 2AgCl + 2NaHO + O_2;$$

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and sulphate of manganese into hydrated peroxide of manganese, with liberation of chlorine: —

$$Mn_2SO_4 + 2NaClO + H_2O = Na_2SO_4 + 2MnHO_2 + Cl_2.$$

Chlorous Anhydride, Acid, and Salts.

(61) Chlorous anhydride. *Sym.* Cl_2O_3; *p.n.* 119; *v.d.* 59·5; □□. — *a.* This gas results from the spontaneous decomposition of chlorous acid, which is a somewhat ill-defined and unstable substance: —

$$2HClO_2 = H_2O + Cl_2O_3.$$

β. It is also produced by the reaction of chloric acid with nitrous acid or anhydride: —

$$2HNO_2 + 2HClO_3 = 2HNO_3 + H_2O + Cl_2O_3.$$

Instead of using preformed chloric acid and nitrous acid or anhydride, in practice we take a mixture of chlorate of potassium, nitric acid, and arsenious anhydride. The nitric acid is first reduced by the arsenious anhydride to the state of nitrous acid, which is the real deoxygenant of the liberated chloric acid: —

$$2HNO_3 + As_2O_3 + 2H_2O + 2KClO_3 = 2HNO_3 + 2KH_2AsO_4 + Cl_2O_3.$$

The reaction is effected by the application of a very gentle heat. The arsenious anhydride may be replaced by tartaric acid or other deoxidising agent. The gas must be collected by displacement.

Chlorous anhydride is a yellowish green gas, permanent in a freezing mixture of ice and salt, but liquefiable by extreme cold. At slightly elevated temperatures, 57° and upwards, it is decomposed with explosion into chlorine and oxygen. It dissolves freely in water or in solutions of the alkaline and earth-alkaline hydrates, gradually forming chlorous acid or chlorites.

(62) Chlorous acid. *Sym.* $HClO_2$; *p.n.* 68·5.—*a.* This acid may be prepared by condensing chlorous anhydride in water, as we have just seen: —

$$Cl_2O_3 + H_2O = 2HClO_2.$$

β. Or by acting upon a chlorite with some diluted acid, such as sulphuric or phosphoric: —

$$2PbClO_2 + H_2SO_4 = 2HClO_2 + Pb_2SO_4.$$

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The acid, or its concentrated solution, is a greenish yellow liquid of great tinctorial power, and having strong bleaching and oxidising properties. It does not decompose the carbonates, but reacts slowly with caustic alkalies and earths to form chlorites.

(63) CHLORITES.—The alkaline and earthy chlorites are formed as above described. They also result from the action of perchloric oxide on bases (vide par. 68). They are, for the most part, soluble, crystallisable, colourless salts, possessed of bleaching properties. The insoluble chlorites of silver, lead, and other metals are produced by double decomposition:—

$$AgNO_3 + KClO_2 = KNO_3 + AgClO_2.$$

The chlorites are decomposed even by carbonic acid.

CHLORIC ACID AND SALTS.

(64) CHLORIC ACID. *Sym.* $HClO_3$; *p. n.* 84·5.—*a.* The acid is liberated from chlorates by the addition of a stronger acid. It is found advantageous to use equivalent quantities of chlorate of barium and sulphuric acid:—

$$2BaClO_3 + H_2SO_4 = 2HClO_3 + Ba_2SO_4.$$

The solution of chloric acid is separated from the insoluble sulphate of barium by filtration, and concentrated by evaporation in vacuo. *β.* This acid also results from the spontaneous decomposition of solutions of hypochlorous acid, chlorous acid, and peroxide of chlorine.

Chloric acid is a colourless syrupy liquid, having a strong acid reaction, and when warm, a pungent chloroïd smell. It is decomposed by organic matter, with charring, and frequently even with ignition. It is somewhat unstable at ordinary temperatures. At 40° it undergoes marked decomposition, and at a boiling heat is rapidly converted into perchloric acid, water, chlorine, and oxygen. It is a very powerful oxidising and bleaching agent. It is decomposed by chlorhydric, sulphydric, and sulphurous acids, with liberation of chlorine.

(65) CHLORATES.—*a.* These salts may be prepared by saturating the acid with bases. Chlorate of barium is usually made by this process. Fluosilicic acid in excess is added to a solution of chlorate of potassium, and the resulting insoluble fluosilicate of potassium separated by filtration from the chloric acid and excess of fluosilicic acid. The two acids are then saturated with carbonate of barium, and the soluble chlorate thus produced, is filtered

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off from the insoluble mixture of carbonate and fluosilicate, and crystallised by evaporation: —

$$2HClO_3 + Ba_2CO_3 = 2BaClO_3 + H_2O + CO_2.$$

β. Zinc, and one or two other metals, dissolve in chloric acid to form chlorates, thus: $HClO_3 + Zn = ZnClO_3 + H$; but a part of the acid always undergoes a more complex decomposition.

γ. Alkaline chlorates are made by boiling solutions of the hypochlorites, or, what comes to the same thing, by passing chlorine into caustic or carbonated alkali, and boiling the resulting liquid: —

$$3KClO = KClO_3 + 2KCl.$$

The chlorate is separated from the chloride by crystallisation. The chlorates are chiefly interesting as sources of oxygen gas. Chlorate of potassium and most chlorates are decomposed by heat into chloride and oxygen, thus: $KClO_3 = KCl + O_3$; but the chlorates of the earth-metals yield oxygen, chlorine, and metallic oxide: $2MgClO_3 = Mg_2O + Cl_2 + O_5$. Prior to the ultimate decomposition of chlorate of potassium, a portion of perchlorate is produced. The fused chlorates are powerful oxidising agents. Mixtures of chlorate with combustible substances, such as sulphur, sulphide of antimony, and sugar, explode violently on the application of heat, or by percussion. Strong sulphuric acid liberates perchloric oxide from the chlorates, and, by its action on mixtures of chlorate with combustible matters, frequently induces combustion. Nitric acid reacts with chlorate of potassium to form nitrate of potassium, perchlorate of potassium, and free chlorine and oxygen gases. Chlorhydric acid produces euchlorine, which is a gaseous mixture of chlorine and perchloric oxide. A mixture of chlorate of potassium and chlorhydric acid is much used for oxidising mineral and organic compounds. All the chlorates are soluble in water, and hence do not precipitate the salts of the heavy metals. Chlorate of potassium, the most important member of the class, is one of the least soluble. Unlike the hypochlorites and the chlorites, the chlorates do not bleach until after the addition of an acid.

Perchloric Acid and Salts.

(66) Perchloric acid. *Sym.* $HClO_4$; *p.n.* 100·5.—*a.* This acid may be prepared by the reaction of certain other acids upon the

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perchlorates. Thus, fluosilicic acid may be added to perchlorate of potassium, and the resulting insoluble fluosilicate of potassium be filtered off from the solution of perchloric acid; or sulphuric, instead of fluosilicic acid, may be employed, and the volatile perchloric acid be distilled off from the fixed sulphate of potassium: —

$$KClO_4 + H_2SO_4 = HClO_4 + KHSO_4.$$

β. By the distillation of chloric acid, as we have already seen.

γ. By the action of sulphuric acid upon chlorate of potassium, as described under the head of perchloric oxide (vide par. 68).

Perchloric acid is a powerful and, at ordinary temperatures, stable acid. Its solutions do not bleach. They dissolve zinc and iron, with evolution of hydrogen, to form perchlorates. They are unaffected by sulphydric and sulphurous acids, which reduce all other oxacids of chlorine. Solutions of the acid may be concentrated by evaporation, until the temperature reaches to about 140°, when aqueous perchloric acid distils over. The most concentrated aqueous acid is an inodorous, colourless, oily liquid, having a sp. gr. 1·65. When the concentrated acid is distilled with several times its volume of strong oil of vitriol, the greater part is decomposed into water, oxygen, and chlorine, but a portion of the dry perchloric acid $HClO_4$ passes over, and condenses into a white crystalline deliquescent solid.

(67) PERCHLORATES.—*a*. These salts are made by reacting on perchloric acid with metals, oxides, hydrates, or carbonates; or on perchlorate of barium with sulphates: —

Formation of perchlorate of barium. $HClO_4 + BaHO = BaClO_4 + H_2O.$

Formation of perchlorate of sodium. $2BaClO_4 + Na_2SO_4 = 2NaClO_4 + Ba_2SO_4.$

β. By the decomposition of chlorates. During the decomposition of chlorate of potassium by heat, and after a considerable evolution of oxygen has taken place, the previously fused salt is observed to assume a pasty condition. If the application of heat be then stopped, the residue will be found to consist principally of perchlorate and chloride of potassium, which two salts may be separated from one another by solution and crystallisation, the perchlorate being much the less soluble: —

$$2KClO_3 = KClO_4 + KCl + O_2.$$

Or the chlorate of potassium may be decomposed by nitric acid: —

$$3KClO_3 + 2HNO_3 = KClO_4 + 2KNO_3 + H_2O + Cl_2 + O_4;$$

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and the resulting nitrate and perchlorate of potassium be separated from one another by solution and crystallisation.

Perchlorate of potassium is sparingly soluble in cold water; but the perchlorates in general are soluble, crystalline, deliquescent salts. They deflagrate, though less violently than the chlorates, when thrown on ignited charcoal. They require a stronger heat than do the chlorates to effect their decomposition into chloride and oxygen. Sulphuric acid liberates perchloric acid from the perchlorates, but not until the temperature is raised to 100°: other acids liberate perchloric acid, only when they form insoluble salts with the bases of the perchlorates. Hence, unlike chlorates, the perchlorates do not assume a yellow colour when acted upon by sulphuric or chlorhydric acid.

Perchloric Oxide and Euchlorine.

(68) Perchloric oxide. *Sym.* Cl_2O_4; *p.n.* 135; *v.d.* 33·75; ⊞.—This very explosive compound may be prepared by the action of strong sulphuric acid upon chlorate of potassium, whereby perchlorate of potassium, acid sulphate of potassium, water, and perchloric oxide are produced:—

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + H_2O + Cl_2O_4.$$

The chlorate should be purified by recrystallisation, fused, after drying, at the lowest adequate temperature, and then finely pulverised. The powder must be added little by little to sulphuric acid, made cool by a mixture of ice and salt, until a pasty mass is produced. This is to be set aside for some time, and afterwards, by means of a water-bath, to be very gently heated in a retort. The evolved gaseous perchloric oxide must be collected by downward displacement. C. Calvert has shown that perchloric oxide, mixed with carbonic acid, may be readily obtained by heating finely powdered chlorate of potassium with crystallised oxalic acid to a temperature of 70°.

Perchloric oxide is a gas of a bright yellow colour, and sweet aromatic smell. Its sp. gr. is anomalous, and corresponds to a four-volume molecule. At the low temperature produced by a mixture of salt and ice, it is condensed into a yellowish highly explosive liquid. Faraday succeeded in solidifying it by means of the intense cold produced by the evaporation of solid carbonic acid and ether. In daylight the gas undergoes spontaneous decomposition into chlorine and oxygen. This decomposition is frequently, and, when induced by elevation of temperature, almost

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invariably, attended by a violent explosion. The contact of highly combustible matters also determines an explosion. Liquid perchloric oxide unites with water at a temperature of 0° to form a solid hydrate. At ordinary temperatures, water dissolves several times its volume of the gas. The solution has a yellow colour, is devoid of acid reaction, bleaches powerfully, and is very unstable, being decomposed into chloric acid, chlorous acid, and other products. Perchloric oxide is absorbed by alkaline solutions, with formation of chlorate and chlorite: —

$$2KHO + Cl_2O_4 = KClO^2 + KClO_3 + H_2O.$$

The molecule of perchloric oxide Cl_2O_4, like the molecule of chlorine Cl_2, seems to be binary or dyadic, and to halve itself in the act of combination. In this manner, the correlations of chlorite and chlorate would correspond with those of chloride and hypochlorite, thus: —

$$\text{Chloride } \left.\begin{matrix}H\\Cl\end{matrix}\right\} \text{ Hypochlorite } \left.\begin{matrix}H\\Cl\end{matrix}\right\} O. \quad | \quad \text{Chlorite } \left.\begin{matrix}H\\ClO_2\end{matrix}\right\} \text{ Chlorate } \left.\begin{matrix}H\\ClO_2\end{matrix}\right\} O.$$

Moreover, the above reaction of perchloric oxide and alkali might be represented similarly to that of chlorine and alkali: —

$$\left.\begin{matrix}H\\K\end{matrix}\right\} O + \left.\begin{matrix}H\\K\end{matrix}\right\} O + 2Cl = \left.\begin{matrix}H\\H\end{matrix}\right\} O + \left.\begin{matrix}K\\Cl\end{matrix}\right\} O + KCl.$$

$$\left.\begin{matrix}H\\K\end{matrix}\right\} O + \left.\begin{matrix}H\\K\end{matrix}\right\} O + 2ClO_2 = \left.\begin{matrix}H\\H\end{matrix}\right\} O + \left.\begin{matrix}K\\ClO_2\end{matrix}\right\} O + KClO_2.$$

(69) EUCHLORINE.—When chlorate of potassium is acted upon by chlorhydric acid, a bright yellow gas, called euchlorine, is liberated. This gas contains chlorine and oxygen in the same proportions as hypochlorous anhydride Cl_2O, but despite its uniformity of composition, it is evidently a mixture, probably of chlorine and perchloric oxide. The following equation is believed to express its formation correctly:—

$$4KClO_3 + 12HCl = 4KCl + 6H_2O + (9Cl + 3ClO_2).$$

This mixed gas has a sweet aromatic smell, and powerful bleaching properties. By passing it through a U-tube immersed in a mixture of salt and ice, the perchloric oxide is separated in the liquid state from the free uncondensed chlorine. According to Millon, the liquid perchloric oxide obtained by cooling euchlorine, differs from the liquid perchloric oxide obtained by means of sulphuric acid and chlorate of potassium, in its somewhat greater stability, in its somewhat higher boiling point, and in the circumstance that, although like the normal compound, it is decomposed

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by alkalies into chlorate and chlorite, yet that, unlike the normal compound, it yields two equivalents of the former for one of the latter salt. Hence, Millon assigns to it the formula Cl_6O_{13},= $3Cl_2O_4$?

$$Cl_6O_{13} + 6KHO = 3H_2O + 4KClO_3 + 2KClO_2.$$

But these differences may possibly be due to differences in the purity of the two bodies. Moreover, perchloric oxide is a very difficult subject to investigate, and the descriptions of different experimentalists vary considerably from one another.

§ II. Bromine.

Symbol Br; *Proportional number* 80; *Density* 80; *Atomic volume* □.

(70) Bromine exists in the form of a bromide, probably bromide of magnesium, in sea-water, and in several saline springs, particularly in those of Kreuznach, Kissingen, and Cheltenham. Common salt generally yields traces of bromine, and native horn-silver from Mexico contains bromide as well as chloride of silver. Bromine has also been detected in the ashes of sea-weed, sponges, sea-mollusks, and of cod-liver oil.

(71) Bromine is prepared by the action of chlorine upon the bromide of magnesium existing in the mother-liquors of sea-water, or rich spring-water, after the separation of most other salts by crystallisation: —

$$MgBr + Cl = MgCl + Br.$$

The bromine thus liberated is dissolved out by ether, and the dark coloured ethereal liquid treated with solution of hydrate of potassium, whereby the bromine is retained in the form of bromide and bromate of potassium, and the decolorised ether fitted for subsequent extractions: —

$$6KHO + Br_6 = 5KBr + KBrO_3 + 3H_2O.$$

After the solution of potash has been sufficiently charged with bromine, it is evaporated and ignited, so as to convert the bromate into bromide: —

$$5KBr + KBrO_3 = 6KBr + O_3.$$

Free bromine may be prepared from this bromide of potassium by

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the action of sulphuric acid and peroxide of manganese, precisely as free chlorine is obtained from chloride of sodium: —

$$2KBr + 2H_2SO_4 + Mn_2O_2 = K_2SO_4 + Mn_2SO_4 + 2H_2O + Br_2.$$

When bromine is required absolutely free from chlorine, it must be prepared from bromide of barium which has been purified from chloride of barium by solution in absolute alcohol. β. Bromine also results from the ignition of certain metallic bromides, especially in the presence of air or oxygen.

(72) Bromine usually exists in the form of a mobile, deep brownish red liquid, having a sp. gr. 2·96. At ordinary temperatures it emits dark red vapours, and is, indeed, so volatile as usually to be kept under a layer of water. It boils at 45°, and solidifies at —19° into a brittle crystalline mass. The smell of bromine is very offensive and irritating, whence its name (*βρῶμος*). Its action on the skin and mucous membrane is acrid and corrosive. The vapour, even when much diluted with air, is irrespirable. At 0° bromine unites with water to form a solid crystalline hydrate, $Br . 5H_2O$, analogous to that of chlorine. At ordinary temperatures, bromine is soluble in about thirty-three times its weight of water, forming a solution having the colour, taste, smell, and chemical properties of the element, modified only by dilution. By exposure to sunlight, this solution is converted into bromhydric acid and oxygen, thus: $Br_2 + H_2O = 2HBr + O$, the decomposition being analogous to that which the solution of chlorine undergoes under similar circumstances. Like chlorine, bromine is a body possessed of active chemical properties. It unites with olefiant gas, sulphurous anhydride, and, indeed, with all substances that combine directly with chlorine, to form compounds of analogous character. Its union with phosphorus, antimony, and tin respectively, is attended by the phenomena of combustion. It readily liberates iodine from its combinations. It displaces hydrogen by equivalent substitution. It is possessed of marked oxidising and bleaching properties. It gives a bright reddish yellow colour with starch.

Bromhydric Acid.

Symbol HBr; *Proportional number* 81; *Density* 40·5; *Atomic volume* □□.

(73) This gas, frequently named hydrobromic acid, and its solution in water, are obtainable by various processes, all of them analogous to those which yield the corresponding acid of chlorine.

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a. Thus, bromhydric gas may be prepared by the action of sulphuric acid upon bromide of potassium: —

$$KBr + H_2SO_4 = HBr + KHSO_4.$$

But sulphuric acid produces a partial decomposition of bromhydric acid, and hence is advantageously replaced by a strong solution of phosphoric acid: —

$$KBr + H_3PO_4 = HBr + KH_2PO_4.$$

The gas must be collected over the mercurial trough. *β*. Bromhydric acid likewise results from the direct union of bromine vapour and hydrogen gas, though not very readily. The combination is best effected by means of platinum wire kept red-hot by the passage of an electric current. *γ*. Bromhydric acid is also produced by the reaction of water upon certain bromides, especially those of phosphorus and antimony: —

$$PBr_5 + 4H_2O = 5HBr + H_3PO_4.$$

This is a frequently used method for preparing bromhydric gas, save that the bromide of phosphorus, resulting from the direct union of phosphorus and bromine, is produced extempore in the presence of water, and so decomposed either in the nascent state, or immediately afterwards. The bromine is distilled over fragments of moist phosphorus, and the vapours transmitted over wet crushed glass. *δ*. Bromhydric acid results from the action of bromine upon very many hydrogenised substances, whether or not attended by the formation of substitution-products: —

$$\overbrace{C_8H_5NO^2}^{\text{Isatin.}} + Br_2 = \overbrace{C_8H_4BrNO_2}^{\text{Bromisatin.}} + HBr.$$

$$\overbrace{C_{14}H_{12}O_2}^{\text{Benzoine.}} + Br_2 = \overbrace{C_{14}H_{10}O_2}^{\text{Benzile.}} + 2HBr.$$

A solution of bromhydric acid is easily prepared by treating bromine-water with a slight excess of sulphydric acid, filtering to separate sulphur, and warming gently to drive off any undecomposed sulphydric acid: —

$$Br_2 + H_2S = 2HBr + S.$$

(74) Bromhydric acid is a colourless gas, having a pungent odour, acrid taste, and marked acid reaction. It fumes in moist air, and is rapidly absorbed by water. It liquefies at $-69°$, and solidifies at $-73°$. It is decomposed by potassium and several other metals, with

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the liberation of half its volume of hydrogen: $HBr + K = KBr + H$. It is decomposed by chlorine, with liberation of bromine, and formation of chlorhydric acid: $HBr + Cl = HCl + Br$.

Solution of bromhydric acid is a colourless, and in its most concentrated state, a fuming liquid, having a sp. gr. 1·29. Its reactions correspond with those of the gas. When boiled it gives off bromhydric gas, and subsequently the dilute aqueous acid.

BROMIDES.

(75) These compounds have not been so minutely studied as have the chlorides. They form a large but not very important class of salts. They are divisible into sub-groups analogous to those of the chlorides; and, as a rule, the members of corresponding chloride and bromide sub-groups correspond very closely in their properties and modes of formation. Thus the dibromides, those of mercury and copper for instance, are quite insoluble in water. The protobromides, those of potassium and cadmium for instance, are soluble, fusible, and, at a high temperature, volatile salts. Bromide of silver, however, is insoluble, like the chloride of that metal, and bromide of lead is nearly insoluble. Moreover, the protobromides of palladium, platinum, and copper, are decomposed at a high temperature. Many hydrated protobromides, those of magnesium and zinc for instance, when heated to redness, break up wholly or partly into bromhydric acid and metallic oxide. The bibromides, stannous bromide for instance, are like the bichlorides readily volatile, with the exception of the bibromides of platinum and palladium, which decompose below a red heat. The sesquibromides, those of iron and aluminum for example, are for the most part volatile, but the hydrated sesquibromides are decomposed by heat into bromhydric acid and metallic oxide. The terbromides, tetrabromides, and pentabromides, are readily volatile compounds, which decompose more or less completely in the presence of water. The terbromide of gold, however, is soluble in water and decomposed by heat.

(76) The bromides may be prepared—*a.* By the direct action of bromine upon a metal, as instanced in the preparation of terbromide of antimony. Hydrated protobromide of iron is made by agitating an excess of iron with bromine and water. Altogether bromine vapour acts less powerfully upon metals than does chlorine gas. Platinum is unaffected by bromine at ordinary temperatures.

β. By the action of bromine upon a metallic oxide, hydrate, or

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carbonate. Bromine displaces the oxygen of many metallic oxides, that of oxide of silver at ordinary temperatures. At a red heat it even displaces the oxygen of the oxides of barium, calcium, potassium, and sodium. Under the same circumstances, with the hydrates or carbonates, we have water, or carbonic anhydride, liberated in addition to the oxygen.

At ordinary temperatures, when bromine acts upon the oxides, or hydrates, or carbonates of the alkali- and alkaline-earth metals, we have produced mixtures of bromide with hypobromite or bromate, which last salts are decomposed by ignition into bromide and oxygen.

γ. By acting upon bromhydric acid with tin, zinc, cadmium, or iron, which respectively displace the hydrogen of the acid to form bromides.

δ. By saturating bromhydric acid with oxides, hydrates, or carbonates. When bromhydric acid reacts upon a peroxide, we have evolution of bromine, precisely as with chlorhydric acid and a peroxide we have evolution of chlorine; moreover, when a bromide is acted upon by sulphuric acid and a peroxide, that of manganese for instance, we always have bromine liberated.

ε. On account of their insolubility, the dibromide of mercury and the protobromides of lead and silver, are readily prepared by precipitation. Free bromine, bromhydric acid and all soluble bromides, give with solution of nitrate of silver a white or yellowish white precipitate of bromide of silver, insoluble in nitric acid.

As a rule, the bromides are more easily decomposed than are the corresponding chlorides when heated in air, or oxygen gas, or with the vapour of water, or in a current of hydrogen. Chlorhydric acid reacts with metallic bromides to form metallic chlorides and bromhydric acid. All bromides, even bromide of silver, are decomposed by chlorine or chlorine-water, with evolution of bromine, which may be recognised by its yellow colour, by its solubility in ether, and by its characteristic reaction with starch. Bromine moreover is liberated from bromides by all oxidating acids, such as the nitric and hypochlorous. Even strong sulphuric acid acts as an oxygenant, is reduced to sulphurous acid, and sets free bromine.

The bromides of the basylous metals unite with the bromides of the chlorous metals, to form well-defined crystalline double salts.

Oxidised Compounds of Bromine.

(77) Our knowledge of these compounds is very imperfect, and the series itself very incomplete. By analogy we should have—

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HBr	Bromhydric acid.
HBrO	Hypobromous acid.
$HBrO_2$	Bromous acid.
$HBrO_3$	Bromic acid.
$HBrO_4$	Perbromic acid.

Bromic acid and its salts are tolerably well known, and the existence of hypobromous acid and salts is generally admitted, but no satisfactory evidence has been obtained with reference to the bromous and perbromic acids.

Hypobromous Anhydride, Acid, and Salts.

(78) When bromine vapour is passed over dry mercuric oxide, a gas, probably hypobromous anhydride Br_2O, is produced. When excess of mercuric oxide is agitated with bromine-water, bromide of mercury and hypobromous acid HBrO, are formed; and by distilling the clear liquid in vacuo, a simple solution of the acid may be obtained. When bromine is added in small quantities to solutions of fixed caustic alkali, colourless liquids are produced, having the bleaching and oxidating properties, as well as the peculiar smell, of the hypochlorites.

Bromic Acid and Salts.

(79) Bromic acid. *Sym.* $HBrO_3$; *p. n.* 129.—This body can be prepared by the action of certain acids upon the bromates. It is advisable to use bromate of barium and sulphuric acid in equivalent quantities, whereby there is produced a precipitate of sulphate of barium and a solution of bromic acid, which may be poured off and concentrated by evaporation:—

$$2BaBrO_3 + H_2SO_4 = 2HBrO_3 + Ba_2SO_4.$$

The concentrated solution of bromic acid is a colourless, somewhat oily liquid, having strongly acidulous, bleaching, and oxidising properties. By ebullition it breaks up into water, oxygen, and bromine. It is decomposed by reducing agents, such as sulphurous and sulphydric acids, with liberation of bromine.

(80) Bromates.—These salts are made—*a.* By saturating bromic acid with bases. *β.* By adding bromine to solutions of fixed alkali, and separating the sparingly soluble bromate from the bromide by crystallisation:—

$$6KHO + Br_6 = 3H_2O + 5KBr + KBrO_3.$$

γ. By adding pentachloride of bromine to a solution of fixed caustic alkali, and crystallising out the bromate from the chloride:—

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$$6KHO + BrCl_5 = 3H_2O + 5KCl + KBrO_3.$$

The bromates are for the most part soluble and crystallisable salts: the mercurous, silver, and lead salts are, however, insoluble. The bromates, like the chlorates, explode when heated or rubbed with combustible matters. Their solutions are decomposed by reducing agents. The salts when ignited give off oxygen and become bromides, as is the case with the bromates of potassium, sodium, mercury, and silver, thus: $KBrO_3 = KBr + O_3$; or they give off bromine and a part of the oxygen, leaving metallic oxides, as happens with the bromates of magnesium, aluminum, and zinc:—

$$2MgBrO_3 = Mg_2O + Br_2 + O_5.$$

(81) CHLORIDE OF BROMINE is a reddish-yellow volatile liquid, prepared by passing chlorine gas through bromine, and condensing the vapours. Its composition is believed to be $BrCl_5$. It is soluble in water, forming a yellowish solution, which may also be produced by passing chlorine into bromine-water. This solution is decomposed by alkalies, as we have just seen, into chloride and bromate. With a small quantity of water, and at a low temperature, chloride of bromine forms a definite crystalline hydrate.

§ III. IODINE.

Symbol I; *Proportional number* 127; *Vapour density* 127; *Atomic volume* □.

(82) Iodine occurs in nature most frequently in combination with sodium, or calcium, or magnesium. These iodides exist in very minute quantities in sea water and in certain mineral springs. The great source of iodine is the ash of sea-weed, technically known as kelp. The ashes of marine zoophytes, mollusks, and even animals much higher in the scale, contain iodine in notable quantity: for instance, it is easily recognisable in cod-liver oil. Iodine has moreover been found in combination with the metals zinc, lead, mercury and silver; it has also been detected in coal. Some varieties of Chili nitre yield a considerable percentage of iodide and iodate of sodium.

(83) *a.* Iodine is made by lixiviating kelp, and concentrating the resulting solution so as to effect a separation of most of the contained salts. From the mother liquor iodine is then procured by

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one of several processes. The most usual method is to add a solution of dicuprous sulphate, or in practice, what comes to the same thing, a mixture of cupric and ferrous sulphates, whereby dicuprous iodide is precipitated, and a variety of iron-alum left in solution:—

$$Fe_2SO_4 + Cu_2SO_4 + NaI = Fe_2Na(SO_4)_2 + Cu_2I.$$

This iodide is then heated with peroxide of manganese and sulphuric acid, whereby iodine is evolved, precisely as by similar treatment we obtain chlorine from chlorides, and bromine from bromides:—

$$Cu_2I + Mn_2O_2 + 2H_2SO_4 = I + 2H_2O + Cu_2SO_4 + Mn_2SO_4.$$

Frequently the precipitation of the iodine as diniodide of copper is dispensed with, and the mother-liquor containing iodide of sodium simply treated with peroxide of manganese and sulphuric acid:—

$$2NaI + Mn_2O_2 + 2H_2SO_4 = I_2 + 2H_2O + Na_2SO_4 + Mn_2SO_4.$$

The sulphuric acid is added first, and the mixture set aside for some time, whereby sulphate of sodium crystallises out, and sulphydric, carbonic, and other gaseous acids are liberated. The acid liquid is then treated with peroxide of manganese in a leaden retort, and the distillation effected at a temperature not much exceeding 100°. The iodine sublimes over, and crystallises in a series of globular condensers. It is purified by a second sublimation.

β. Iodine also results from the ignition of certain metallic iodides, and from the decomposition of oxidised compounds of iodine.

(84) Iodine is a friable, black-coloured, metallic-looking solid, having a sp. gr. 4·94. It is scarcely translucent, but when sufficiently thin, transmits violet light. Its crystals occur in forms belonging to the right prismatic system, the primary form being an acute rhombic octohedron. It fuses at 107° into a deep brown liquid, and boils at 175° into a beautiful violet coloured vapour, whence its name (*ἰώδης*). It is sensibly volatile even at ordinary temperatures. Its taste is acrid, and its smell chloroïd or marine. It stains the skin and other organic tissues of a yellowish brown colour. Unlike chlorine and bromine it does not form a definite hydrate. It is scarcely soluble in water, but yet sufficiently so to form a pale brown solution. It is however soluble in very many liquids. Some of these solutions,

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as the ethereal and alcoholic, have the deep brown colour of liquid iodine. But the solutions in chloroform, petroleum, bisulphide of carbon, &c., have the beautiful violet colour of the vapour. Iodine combines directly with nearly all the substances, simple and compound, that unite directly with chlorine and bromine, though for the most part less violently. Its union with phosphorus or antimony, however, is attended with combustion. Iodine has the characteristic property of forming a deep blue compound with starch. This colour disappears at a temperature below 100°, but reappears on cooling. Iodine and its solution in water are not possessed of bleaching properties, or at least to a very trifling extent only.

Like chlorine and bromine, iodine is capable of directly replacing the hydrogen of very many compounds by equivalent substitution, thus: $C_6H_7N + I_2 = C_6H_6IN . HI$.

Iodhydric Acid.

Symbol HI; *Proportional number* 128; *Density* 64; *Atomic volume* □□.

(85) This acid may be prepared by all the processes used for making chlorhydric and bromhydric acids. *α.* By the action of phosphoric or dilute sulphuric acid upon an iodide, preferably iodide of barium:—

$$2BaI + H_2SO_4 = 2HI + Ba_2SO_4.$$

The solution of iodhydric acid can be poured off from the precipitated sulphate of barium. Any excess of sulphuric acid would decompose the nascent iodhydric acid, so that equivalent quantities of the reagents must be employed. *β.* Iodhydric acid may also be obtained by passing iodine vapour, together with hydrogen gas, through a red-hot tube, or over spongy platinum gently heated. *γ.* Iodhydric acid is readily produced by the action of water upon certain iodides. Thus with water and teriodide of phosphorus, which last compound may be prepared extempore by the mixture of its two constituents, we have produced iodhydric and phosphorous acids:—

$$PI_3 + 3H_2O = 3HI + H_3PO_3.$$

One of the best methods of obtaining iodhydric acid consists in heating together, in a retort, water, iodide of potassium, iodine and phosphorus. The reaction is,

$$2KI + PI_5 + 4H_2O = 7HI + K_2HPO_4.$$

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δ. Iodhydric acid also results from the direct action of iodine upon various hydrogenised bodies. A solution of iodhydric acid is readily made by acting on iodine and water with sulphydric acid:—

$$I_2 + H_2S = 2HI + S.$$

If, instead of gaseous sulphydric acid, liquid persulphide of hydrogen be employed, a yellowish brown liquid is produced which decomposes in the presence of water. If the reaction with water be effected in a bent sealed tube, the gas evolved in one limb may be readily condensed as a mobile liquid in the other:—

$$I_2 + H_2S = 2HI + S_2.$$

(86) Gaseous iodhydric acid is best collected by downward displacement. It cannot be collected over water, and can be retained for a very short time only over mercury. The gas is colourless, has a sour smell and taste, reacts strongly acid with test paper, fumes in moist air, and is very soluble in water. The liquid compound has a yellowish colour, and congeals at a temperature of −55°. Gaseous iodhydric acid, or its solution in water, is decomposed by the metals potassium, zinc, iron, &c., with evolution of hydrogen, and formation of metallic iodides. Chlorine, bromine, nitric acid, hypochlorous acid, and all oxidising agents, decompose iodhydric acid with liberation of iodine. Sulphuric acid, and even sulphurous anhydride, act in this manner as oxygenants:—

$$H_2SO_4 + 2HI = H_2SO_3 + H_2O + I_2.$$
$$SO_2 + 4HI = S + 2H_2O + I_4.$$

A solution of iodhydric acid undergoes spontaneously a partial decomposition into iodine and hydrogen. The iodine dissolves in the undecomposed acid, forming a deep brown solution. By exposure to air it is decomposed more rapidly, with production of water and free iodine. The strongest solution of iodhydric acid is a colourless fuming liquid. It has a sp. gr. 1·7, boils at about 125°, and may be distilled over unchanged.

Iodides.

(87) These salts correspond very closely in their general characters and modes of formation to the bromides and chlorides, and present us with the same sub-groups. As a rule, they are less volatile, more insoluble, and more easily decomposed. The iodides of the heavy metals, more particularly those of lead and mercury, are remarkable for the brilliancy of their colours. The

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iodides of tin, antimony, and arsenic, like the chlorides and bromides, are decomposed by water at ordinary temperatures. The hydrated iodides of magnesium, zinc, and aluminum are, like chlorides and bromides, decomposed by heat into metallic oxide and hydracid—in this case iodhydric. In addition to the iodides of palladium, platinum, and gold, iodide of silver, unlike its chloride and bromide, is decomposed at a red heat. All iodides, except those of the alkali- and alkaline-earth groups, are decomposed at a red heat by a current of hydrogen. The iodides, with the exception of those last mentioned, and those of lead and bismuth, are also decomposed by oxygen gas at a red heat. All iodides are decomposed by most mineral acids, either with formation of iodhydric acid, as when phosphoric and dilute sulphuric acids are employed, or more frequently with formation of free iodine owing to oxidation, as when nitric, strong sulphuric, chloric, and iodic acids are employed. The iodides are scarcely affected by aqueous chlorhydric acid. Chlorine and bromine, or their solutions in water, immediately set free iodine, recognisable by the deep blue colour it imparts to a decoction of starch, or by the violet colour it imparts to bisulphide of carbon. An excess of chlorine destroys the colour at first produced. Aqueous solutions of the iodides, particularly when concentrated, dissolve iodine freely, forming deep brown-coloured liquids.

(88) The iodides are obtained by the same processes that yield us the chlorides and bromides. *a.* By the direct action of iodine upon a metal. In this way the two iodides of mercury and the hydrated protiodides of iron and zinc are frequently prepared. *β.* By the action of iodine upon certain metallic oxides, hydrates, or carbonates. Iodine displaces the oxygen of the oxides of potassium, sodium, barium, and calcium, at a red heat, and that of oxide of silver at ordinary temperatures. When solutions of caustic or carbonated alkali are treated with iodine, mixtures of iodide and iodate are produced, which last salt is decomposed by heat into iodide and oxygen. Iodine and peroxide of barium, when mixed with water, decompose into iodide of barium and oxygen, thus:

$$I_2 + Ba_2O_2 = 2BaI + O_2.$$

γ. By acting on iodhydric acid with certain metals, such as potassium, zinc, and iron, whereby a replacement metal for hydrogen is effected. *δ.* By saturating iodhydric acid with oxides, hydrates, or carbonates. With a peroxide and iodhydric acid we have iodine liberated, precisely as from chlorhydric acid we obtain chlorine, and from bromhydric acid bromine. All

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iodides when acted upon by sulphuric acid and a peroxide give off iodine. *ε.* The insoluble iodides are prepared by adding a solution of an alkaline iodide to a solution of the heavy metals. In this way the iodides of lead, silver, gold and mercurosum are precipitated of a yellow or yellowish colour; that of mercurium, scarlet; that of cuprosum, greenish white; those of bismuth and platinum, brown; that of palladium, black. The iodides of the basylous metals, and of hydrogen, combine with the iodides of the chlorous metals, to form well-defined crystalline double salts.

Oxidised Compounds of Iodine.

(89) By analogy we should have the following acids and oxides or anhydrides:—

HI	Iodhydric acid	I_2	Iodine.
HIO	Hypiodous acid	I_2O	Iodous oxide.
		I_2O_2	Iodic oxide.
HIO_2	Iodous acid	I_2O_3	Iodous anhydride.
		I_2O_4	Periodic oxide.
HIO^3	Iodic acid	I_2O_5	Iodic anhydride.
		I_2O_6	Hyperiodic oxide.
HIO_4	Periodic acid	I_2O_7	Periodic anhydride.

The iodic and periodic acids and anhydrides are well known. The existence of periodic oxide has been rendered extremely probable by the experiments of Millon. Moreover, some evidence has been adduced in favour of the existence of iodous oxide, and hypiodous or iodous acid.

Iodic Anhydride, Acid, and Salts.

(90) Iodic anhydride. *Sym.* I_2O_5; *p. n.* 334.—This compound is produced by heating iodic acid to a temperature of 170°, when it breaks up into iodic anhydride and water:—

$$2HIO_3 = H_2O + I_2O_5.$$

It occurs as a white crystalline solid, which at the temperature of boiling oil fuses, and resolves itself into oxygen and iodine.

(91) Iodic acid. *Sym.* HIO_3; *p. n.* 176.—This acid may be prepared—*α.* By acting upon the anhydride with water:—

$$I_2O_5 + H_2O = 2HIO_3.$$

β. By the action of certain acids upon the iodates. It is preferable to use sulphuric acid and iodate of barium in equivalent quantities. *γ.* By boiling strong nitric acid upon iodine, evapo-

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rating to dryness, redissolving, and crystallising. δ. By acting upon iodine and water with chlorine:—

$$I + Cl_5 + 3H_2O = HIO_3 + 5HCl.$$

The chlorhydric acid may be removed by oxide of silver.

Iodic acid crystallises in white, or yellowish white, translucent six-sided tables. It is very soluble in water, and slightly so in alcohol. Its aqueous solution keeps tolerably well when protected from deoxidating agents. The acid is a powerful oxygenant. When heated with combustible bodies it is rapidly decomposed, but there is no explosion. Sulphurous acid, sulphydric acid, phosphorous acid, stannous salts, and most reducing agents, decompose iodic acid with liberation of iodine. Several organic substances, particularly morphia, also decompose iodic acid and set free iodine. Iodic acid when heated, first loses water to become the anhydride, and then breaks up into iodine and oxygen.

Iodic and iodhydric acids mutually decompose one another with separation of iodine:—

$$5HI + HIO_3 = 3H_2O + I_6.$$

(92) IODATES.—These salts are made by processes analogous to those which furnish us with the chlorates and bromates. *a.* By saturating iodic acid with bases. *β.* By adding iodine to soluble hydrates or carbonates, and crystallising the sparingly soluble iodate from the very soluble iodide:—

$$6KHO + I_6 = 3H_2O + 5KI + KIO_3.$$

Or the separation may be effected by alcohol, which dissolves the iodide and leaves the iodate. *γ.* By dissolving iodine in alkali, and treating the mixture with chlorine gas:—

$$6KHO + I + Cl_5 = 3H_2O + 5KCl + KIO_3.$$

The iodate is then to be separated from the chloride by crystallisation. The iodates are sparingly soluble crystalline salts. Some of them, like their corresponding chlorates and bromates, are decomposed by heat into iodide and oxygen, thus: $KIO_3 = KI + O_3$. Others, like their corresponding chlorates and bromates, break up into oxide, oxygen, and the halogen, in this case iodine:—

$$2MgIO_3 = Mg_2O + I_2 + O_5.$$

The iodates, like the chlorates and bromates, explode when heated or rubbed with combustible bodies. Their solutions are decomposed by most reducing agents, with liberation of iodine.

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The anhydro-iodates are interesting, as being the only well-defined illustrations of anhydro-salts produced from monobasic acids. We have,

$2KIO_3$ or $K_2O . I_2O_5$. . Normal iodate of potassium.
$2KIO_3 . I_2O_5$ or $K_2O . 2I_2O_5$. . Biniodate of potassium.
$2KIO_3 . 2I_2O_5$ or $K_2O . 3I_2O_5$. . Teriodate of potassium.

PERIODIC ANHYDRIDE, ACID, AND SALTS.

(93) PERIODIC ANHYDRIDE. *Sym.* I_2O_7; *p. n.* 366.—By heating periodic acid to a temperature of 160°, water is given off, and a white crystalline mass obtained, which is believed to be the anhydride. This substance, when further heated, gives off oxygen to produce iodic anhydride, which ultimately breaks up into iodine and oxygen.

(94) PERIODIC ACID. *Sym.* HIO_4; *p. n.* 192.—*a.* This compound may be prepared by acting upon the anhydride with water:—

$$I_2O_7 + H_2O = 2HIO_4.$$

β. By treating a periodate, preferably periodate of lead, with sulphuric acid, taking care to avoid any excess:—

$$2PbIO_4 + H_2SO_4 = 2HIO_4 + Pb_2SO_4.$$

The solution of periodic acid is poured off from the insoluble sulphate of lead, evaporated, and crystallised. *γ.* Periodic acid has a tendency to form basic salts, and when certain periodates, that of silver, for instance, are boiled or digested in water, they break up into free periodic acid, and insoluble basic periodates.

Periodic acid occurs in colourless oblique rhombic prisms, permanent in dry air, deliquescent in moist air, and very soluble in water. The crystals fuse at 130°, and decompose at 160°, into water and the anhydride. The acid and its solution act as powerful oxygenants, usually with liberation of iodine.

(95) PERIODATES. — *a.* These salts may be, but seldom are, prepared by saturating the acid with bases. *β.* Periodate of sodium is usually made by passing chlorine gas through iodate of sodium dissolved in solution of caustic soda. The sparingly soluble periodate is deposited on evaporation:—

$$NaIO_3 + 2NaHO + Cl_2 = NaIO_4 + H_2O + 2NaCl.$$

From this salt the insoluble iodates can be prepared by precipitation: many of the precipitated salts are basic. It is observable that while iodic acid exhibits a tendency to form anhydro-

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salts, periodic acid is remarkable for its production of basic salts. The basic periodates appear to arise from the replacement of the water of crystallisation, by a metallic oxide or hydrate, thus:—

$H IO_4 . 2H_2 O$. . . Periodic acid.
$K IO_4 . 2H_2 O$. . . Periodate of potassium (monobasic).
$Ba IO_4 . BaH O . H_2 O$. Periodate of barium (bibasic).
$Pb IO_4 . Pb_2 O . H_2 O$. Periodate of lead (terbasic).

Most periodates are insoluble, or somewhat sparingly soluble. When heated, they either give off oxygen only, and leave metallic iodide, or they give off both oxygen and iodine, and leave metallic oxide, or mixtures of metallic oxide and iodide. They detonate when heated with combustible bodies.

Chlorides and Bromides of Iodine.

(96) Protochloride of Iodine. *Sym.* ICl; *p. n.* 162·5.—This is an unimportant substance, made by passing chlorine over iodine until a liquid compound is produced. It may also be obtained by distilling iodine with chlorate of potassium. It is a deep brown-coloured deliquescent liquid, very soluble in water. When heated it breaks up into terchloride and free iodine.

Terchloride of Iodine. *Sym.* ICl_3; *p. n.* 233·5.—This substance is prepared by the prolonged action of an excess of chlorine upon dry iodine. It also results from the action of chlorhydric acid upon iodic acid. It occurs crystallised in orange-coloured needles. It dissolves in water, but undergoes a partial decomposition.

Bromides of Iodine.—With bromine, iodine forms a solid, volatile, crystalline compound, probably a protobromide IBr, and with excess of bromine, a dark brown liquid, soluble in water, probably a pentabromide IBr_5.

§ IV. Fluorine.

Symbol F; *Proportional number* 19; *Density* 19?; *Atomic volume* □?

(97) The beautiful crystalline minerals, fluor-spar, or fluoride of calcium, and cryolite, or fluoride of aluminum, constitute the principal sources of fluorine. Fluoride of cerium, a somewhat rare mineral, is also found tolerably pure. Fluorides of various kinds,

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moreover, enter to a greater or less extent into the composition of many complex minerals, such as yttrocerite, apatite, lepidolite and hornblende. Traces of fluorine, as shown more particularly by the recent experiments of Wilson and of Nicklès, are very widely distributed in nature. Thus, fluorine has been detected in feldspar and many primary rocks, in fossil and recent bones, in teeth, in urine, in blood, in milk, and in the siliceous stems of grasses and equisetums.

By reason of its active chemical properties, fluorine has never yet been satisfactorily examined, or scarcely obtained, in the free state. No sooner is it liberated from one combination than it enters into another. It appears to be a gas, having the general characters of chlorine, but being still more energetic in its reactions. It is particularly remarkable for the rapidity of its action on silicated compounds, including glass, even so as to prevent the employment of glass vessels for its preparation.

The most recent experiments on the isolation of fluorine are those of Fremy, who submitted fused fluoride of potassium to electrolysis, and thereby obtained a gas which rapidly attacked platinum, decomposed water with formation of fluorhydric acid, and displaced iodine from its metallic combinations. Several chemists, including Fremy, have obtained a similar gas by the action of chlorine or oxygen upon heated fluorides. The Messrs. Knox, in their experiments, employed vessels of fluor-spar, a compound already saturated with fluorine, and upon which the gas was consequently without action.

Fluorhydric Acid.

Symbol HF; *Proportional number* 20; *Density* 10? *Atomic volume* □□?

(98) *a.* This gas is prepared by the action of sulphuric acid upon fluoride of calcium. The reaction is analogous to that which yields us chlorhydric, bromhydric, and iodhydric acids:—

$$2CaF + H_2SO_4 = 2HF + Ca_2SO_4.$$

Finely powdered fluor-spar is mixed with sulphuric acid, and the resultant pasty mass gently heated in a leaden or platinum retort, to which a leaden or platinum U-tube condenser is attached. A very concentrated aqueous acid distils over into the U-tube, which should be surrounded by a freezing mixture. When this liquid product is treated with phosphoric anhydride, the water is retained

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and the gaseous acid liberated, which may be collected over perfectly dry mercury; but according to Fremy, the phosphoric anhydride acts very imperfectly. An aqueous solution of fluorhydric acid may be obtained by receiving the product of the reaction of sulphuric acid and fluor-spar directly into water, contained in a vessel of lead or gutta-percha. β. Dry fluorhydric gas is best obtained by igniting the fluorhydrate of fluoride of potassium :—

$$KF.HF = KF + HF.$$

γ. From ignited fluoride of lead, and other fluorides, we may obtain fluorhydric acid by the action of hydrogen, precisely as we can obtain chlorhydric acid from metallic chlorides:—

$$PbF + H = HF + Pb.$$

δ. Fluorhydric acid also results from the decomposition of certain fluorides by water. Thus fluoride of silicon reacts with water to form silicofluoric and silicic acids:—

$$3SiF_4 + 3H_2O = 2(2HF.SiF_4) + H_2SiO_3;$$

and the silicofluoric acid gradually breaks up into fluoride of silicon, which evaporates, and fluorhydric acid, which remains in solution.

(99) Fluorhydric gas is colourless, has a strong acid reaction, fumes in moist air, and is rapidly absorbed by water. When absolutely dry, it has but little action on glass. According to Fremy, it condenses at — 20° into a very mobile liquid, which reacts violently with water, forms white fumes in the air, and attacks glass readily. The concentrated aqueous acid is a colourless mobile liquid, which boils at 15°; the fumes are highly caustic and irritating, and the liquid itself is a most virulent caustic. Its union with excess of water is accompanied by a hissing noise and a considerable development of heat. The most concentrated acid has a sp. gr. 1·06. The acid of greatest density, namely, 1·15, is more dilute, and consists of $HF.2H_2O$. This compound boils at 120°, and distils over unchanged. Diluted fluorhydric acid dissolves many metals with evolution of hydrogen. It dissolves silica and several other anhydrides which are insoluble in all ordinary menstrua. It speedily corrodes and dissolves glass. The process of etching on glass is performed by means of fluorhydric acid. The glass plate or tube to be etched is first coated with a thin layer of beeswax. Through this layer, tracings are made by a sharp instrument, so as to expose certain lines or portions of the glass. The corrosion of the traces is then speedily effected by the action of the vapour or solution of fluorhydric acid.

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Fluorides.

(100) The fluorides may be prepared by several processes corresponding to those which yield us the chlorides, bromides, and iodides. *a.* By acting on certain metals, potassium, iron, and zinc, for instance, with fluorhydric acid, whereby a replacement of metal for hydrogen is effected; or some metallic fluoride may be used instead of fluorhydric acid, and a different metal be substituted for the original one:—

$$Sb + 3HgF = SbF_3 + Hg_3.$$

β. By treating metallic oxides, hydrates, or carbonates with fluorhydric acid, or its solution in water. When the required fluoride is readily volatile, the nascent fluorhydric acid resulting from the action of sulphuric acid on fluor-spar may be rendered available:—

$$SnO_2 + 4CaF + 2H_2SO_4 = 2H_2O + SnF_4 + 2Ca_2SO_4.$$

γ. The insoluble fluorides of lead, barium, and calcium may be made by precipitating soluble fluorides with solutions of salts of the metals:—

$$PbNO_3 + KF = KNO_3 + PbF.$$

Precipitated fluoride of calcium is very transparent, and has a refractive index so near to that of water, as to render it scarcely visible when diffused in that liquid. The addition of ammonia renders it more easily perceptible.

The fluorides, as a class, have been but imperfectly studied. They are divisible into the same sub-groups as are the chlorides, bromides, and iodides. Most of them are easily fusible, and those of the chlorous metals volatile. Fluor-spar, whence the name fluorine, was so called on account of its ready fusibility and its properties as a flux for silica (*fluo*). The dry fluorides are not decomposed by ignition, but in the presence of aqueous vapour they yield metallic oxide and fluorhydric acid. They are decomposed when treated with sulphuric, nitric, chlorhydric and phosphoric acids, fluorhydric acid being liberated. They are decomposed by chlorine, with liberation of fluorine. The fluorides of silver and alkali-metal are readily soluble in water; but most other fluorides are insoluble, or sparingly soluble. The solutions of fluorides are decomposed by evaporation, and yield crystals of the original salts in combination with fluorhydric acid, the mother-liquor being rendered alkaline. Solutions of fluorides cannot be preserved in

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glass vessels, owing to their reaction with silica. Many chlorous fluorides unite with basylous fluorides to form definite double salts. Fluorhydric acid also unites with metallic fluorides to form acid or hydrogen salts, as above alluded to. The compounds of this class are soluble in water, and have an acid reaction to litmus. There are no known oxides of fluorine or of fluorhydric acid.

§ V. The Halogen Group of Elements.

(101) Fluorine, Chlorine, Bromine, Iodine.—These four substances have one marked property in common, a property not pertaining to any other element with which we are acquainted, namely, that of uniting with hydrogen in the proportion of atom to atom, gaseous atomic volume to gaseous atomic volume. The combinations, moreover, take place without any condensation; while the resulting compounds are powerful acids, and exhibit a striking general resemblance in their properties. They are all gaseous, all condensible, all fuming, all soluble in water, and all result from similar reactions. Chlorine, bromine, and iodine present a marked similarity and gradation of properties. Fluorine is separated from the other members of the group by certain specialities. The atomic weights, which also express the vapour-densities referred to hydrogen, form a remarkable sequence:—

Cl	35·5	
Br	80·0	mean $= 80{\cdot}8 = \frac{242{\cdot}5}{3}$
I	127·0	
Sum	242·5	mean difference = 44 ?

The atomic weight of fluorine, or 19, is rather more than half that of chlorine. At ordinary temperatures, chlorine is a gas, bromine a liquid, iodine a solid. Liquid chlorine boils at — 60°, bromine at 63°, iodine at 175°. The degree of opacity increases regularly. Liquid chlorine is transparent, liquid bromine only when in extremely thin strata, liquid iodine opaque. Solid iodine is possessed of an almost metallic opacity, brilliancy, and colour. Gaseous chlorine is yellowish, gaseous iodine purple, and gaseous bromine intermediate, or orange red. The sp. gr. of liquid chlorine is 1·33, of liquid bromine 2·97, and of solid iodine 4·95. Hence chlorine, bromine, and iodine, when in the liquid or solid state, have sensibly the same atomic volume, namely, 26. Bromine and iodine have sensibly the same atomic heat, 6·7 and 6·8 respectively.

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All four elements in the free state manifest powerful affinities: fluorine, however, appears to be by far the most energetic. In the compounds of the halogens with hydrogen or metal, we notice a sequential alteration of the force with which the hydrogen or metal is retained. Thus iodhydric acid is somewhat unstable, and is decomposed by both chlorine and bromine. Bromhydric acid is more stable, and though decomposible by chlorine, resists the action of iodine. Chlorhydric acid results from the direct union of its constituents at ordinary temperatures, is extremely stable, and resists the action both of bromine and of iodine. The tendency of bromine to unite with the highly basylous metals, is greater than that of iodine; and the tendency of chlorine greater than that of bromine. Thus Field has shown that bromide of silver, when agitated with iodide of potassium, becomes bromide of potassium; while chloride of silver agitated with bromide and, *a fortiori*, with iodide of potassium, becomes chloride of potassium. Chlorine, bromine, and iodine are capable of replacing hydrogen by equivalent substitution in a great variety of compounds, mineral and organic; in the latter more especially, with but a slight modification in the properties of the original bodies. Fluorine also has been made to replace hydrogen in some cases, though by an indirect process only. Analogous fluorides, chlorides, bromides, and iodides, whether anhydrous or hydrated, are for the most part isomorphous. The chloride, bromide, and iodide of hydrogen, or of metal, yield a large number of corresponding oxides, as we have seen. There are no oxidised compounds of fluorhydric acid or of metallic fluoride. Fluorine, moreover, is distinguished from the other three members of this group, by its greater tendency to react on, and dissolve, certain mineral anhydrides which resist the action of most other solvents, and by its greater tendency to form insoluble salts. Fluoride of silver, however, is very soluble, although the chloride, bromide, and iodide are quite insoluble. The fluorides, chlorides, bromides, and iodides of mercury and of lead are insoluble, or sparingly soluble.

(102) All four elements are remarkable for the number and variety of double haloid salts to which they give origin. These salts usually contain a decidedly chlorous and a decidedly basylous metal. Most of them are soluble in water, but are decomposed by a great excess of water, or by prolonged boiling. Some of these double salts are of great beauty, such as the potassio-chlorides of mercury, platinum, and gold. In some salts we have two different halogens united with the same, or with two different

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metals. A great number of acid, or hydrogen, double salts also exist, as is particularly manifested by the fluorine compounds. But many chlorhydrates of chlorides have been described, and the existence of several others, such as those of platinum, gold, and tin, is undeniable. The following is a list of the principal hydracid fluorides and chlorides, and of the double fluorides and chlorides of potassium. Bromine and iodine compounds are introduced when they differ in composition from the chlorine compounds; and, in a similar manner, the salts of other metals than potassium are introduced when they differ from the potassium compounds. To nearly every potassium double salt there are related corresponding barium, strontium, calcium, sodium, lithium, and ammonium double salts: —

Protocompounds.	*Protocompounds.*	*Sesquichlorides, &c.*
K F . H F	K I . 2Zn I	2K Cl . Fe_2Cl_3
Na F . H F	H Cl . 2Hg Cl	2K Cl . R_2Cl_3
K F . Zn F	H I . 2Hg I	2K Cl . Ru_2Cl_3
K Cl . Zn Cl	K Cl . 2Hg Cl	3K F . Fe_2F_3
K Cl . Cd Cl	K I . 2Hg Cl	3NaF . Al_2F_3
K F . Fe F	K I . 2Hg I	3K Cl . Ir_2Cl_3
K F . Cu F	K I . 3Hg Cl	*Terchlorides, &c.*
K Cl . Cu Cl	K Cl . 4Hg Cl	H F . BF_3
Pb Cl . Pb F	2K Cl . Cu_2Cl	K Cl . $AuCl_3$
H I . Pb I	2K I . Pb I	2K Cl . $SbCl_3$
K Br . Pb Br	3K I . 2Pb I	2K Cl . $BiCl_3$
H I . Hg I	*Bichlorides, &c.*	3K Cl . $SbCl_3$
K Cl . Hg Cl	K Cl . $PtCl_2$	*Tetrachlorides, &c.*
H Cl . Ag Cl	K Cl . $IrCl_2$	2H F . SiF_4
Na Cl . Ag Cl	K Cl . $OsCl_2$	2K F . SiF_4
K I . Ag I	K I . 2Sn I_2	2H F . TiF_4
K Cl . Pd Cl	2K Cl . $SnCl_2$	2H Cl . $TiCl_4$
K Cl . Pt Cl	Sn Cl_2. Sn I_2	2K Cl . $SnCl_4$

Fluorides and chlorides form corresponding isomorphous compounds with certain phosphates, as illustrated particularly in the apatites and wagnerites: —

$3Ca_3PO_4$. Ca F	Mg_3PO_4 . Mg F
$3Ca_3PO_4$. Ca Cl	Mg_3PO_4 . Mg Cl
$3Ca_3PO_4$. $Ca\{^{F}_{Cl}$	Mg_3PO_4 . $Mg\{^{F}_{Cl}$

The haloid salts unite with 1, 2, 3, 4, 5, or 6 atoms of constitution or crystallisation water. When this water is replaced wholly or partly by metallic oxide or hydrate, we obtain basic or oxihaloid salts, such as the basic oxichlorides. These salts seem to be altogether different in their characters from certain chloraldehyds, such as Cl_2SO_2 and Cl_3PO, which have also been called oxichlorides.

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CHAPTER III.

(103) Elements of which the single atoms unite respectively with two atoms of hydrogen, *i.e.* one gaseous atomic volume of each element with two gaseous atomic volumes of hydrogen, namely, oxygen, sulphur, selenium, and tellurium. The single atom of any one of these elements is usually equivalent to two atoms of a halogen element, or of hydrogen.

§ I. Oxygen.

Symbol O; *Proportional number* 16; *Density* 16; *Atomic volume* □.

(104) Oxygen is the most abundant of all the elements. It forms eight-ninths of water, nearly one-fourth of the air, and about one-half of silica, chalk, and alumina, the three most plentiful constituents of the earth's surface. With a few exceptions only, of which the principal are rock-salt, fluor-spar, blende, galena, and pyrites, it enters into the constitution of all important rocks and minerals. Independently of its existence in the water of the tissues, it is an essential constituent of all living organisms. It is absorbed by animals during respiration, and evolved in the free state by growing vegetables when exposed to sunlight. The oxygen of the atmosphere is mechanically mixed with the nitrogen and other constituents, but is chemically free or uncombined. Oxygen gas was discovered by Priestley in 1774, and a year later by Scheele.

(105) *a.* Oxygen gas may be prepared by applying a greater or less degree of heat to various oxidised substances, such, for instance, as the oxides of mercury, silver, gold, and platinum; the peroxides of hydrogen, barium, lead, and manganese; and the chlorates, nitrates, bichromates, &c., of potassium and other bases.

a. Oxide of mercury is interesting as being the substance from which oxygen was originally obtained. By heating it in a flask, it breaks up into mercury vapour, which may be condensed in a receiver, and oxygen gas, which may be collected over water: $Hg_2O = Hg_2 + O$.

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b. Peroxide of manganese is a very cheap source of oxygen when large quantities are required. The substance should be heated to redness in an iron bottle, whereby oxygen gas is given off, and a lower oxide of manganese left behind: —

$$3Mn_2O_2 = 2Mn_3O_2 + O_2$$

c. Peroxide of barium, when strongly heated, gives up one-half its oxygen to produce baryta: $Ba_2O_2 = Ba_2O + O$. By passing a current of moist air over the less heated baryta, it absorbs oxygen to re-form the peroxide, which a stronger heat again decomposes; so that, by repetitions of the process, a small quantity of the peroxide can, as was shown by Boussingault, furnish an indefinitely large quantity of oxygen.

d. But chlorate of potassium constitutes the most generally available source of the gas. When strongly heated in a flask of hard glass, it melts, gives off the whole of its oxygen, and leaves a residue of chloride of potassium: —

$$KClO_3 = KCl + O_3$$

The temperature required to effect this decomposition completely is so high, that the flask, though made of difficultly fusible glass, usually becomes softened, and yields to the pressure of the gas, which at last forces an opening through its side or bottom. It is found that the chlorate gives off its oxygen at a much lower temperature when mixed with about one-eighth of its weight of some metallic oxide, such as that of copper, or iron, or manganese. Under these circumstances, the salt does not fuse, but the resulting gas is less pure than when the unmixed chlorate is employed.

β. Oxygen may also be prepared by the action of sulphuric acid, at a moderate temperature, upon certain highly oxidised compounds, such as the peroxides of lead and manganese, the bichromate and permanganate of potassium, &c. These reactions are seldom employed for the purpose of obtaining free oxygen gas, but are extremely convenient as means for affording oxygen to various other bodies, or, in other words, for oxidising them. Thus chlorhydric acid HCl, when treated with sulphuric acid and permanganate of potassium, becomes hypochlorous acid HClO. Alcohol C_2H_6O, when treated with sulphuric acid and peroxide of manganese, yields aldehyd C_2H_4O, and water H_2O. Cuminic acid $C_{10}H_{12}O_2$, when treated with sulphuric acid and bichromate of potassium, yields insolinic acid C_9H_8O, plus carbonic anhydride CO_2,

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plus two atoms of water $2H_2O$. The reactions *quoad* the evolution of oxygen are as follows:—

$$H_2SO_4 + Mn_2O_2 = Mn_2SO_4 + H_2O + O$$
$$2H_2SO_4 + KMn_2O_4 = KMn_2(SO_4)_2 + 2H_2O + O_2$$
$$4H_2SO_4 + K_2Cr_4O_7 = 2\{KCr_2(SO_4)_2\} + 4H_2O + O_3$$

γ. Oxygen may be obtained by the electrolysis of water, which is effected by immersing the platinum terminals of a galvanic battery into water holding sulphuric acid, or hydrate of potassium, or some saline compound, in solution. The oxygen is liberated at the positive pole, or that which communicates with the platinum plate of the battery. Hence oxygen is said to be an electro-negative substance, as an inference from the law that "oppositely electrified bodies attract one another."

δ. When fresh mint, or parsley, or other active leafy plant, is immersed in carbonic acid water and exposed to sunlight, oxygen is liberated from the leaves in considerable quantities. The experiment is best conducted in a tall inverted cylinder, so that the oxygen gas may collect in its upper part, by displacement of the carbonic acid water which should originally fill the vessel.

ε. There are numerous other reactions which serve to liberate oxygen, but they are not employed as means for the preparation of the gas. Some of them, however, are very interesting. Thus when oxide of silver reacts with peroxide of hydrogen, there are produced water, metallic silver, and oxygen:—

$$H_2O_2 + Ag_2O = H_2O + Ag_2 + O_2.$$

(106) Oxygen is colourless, tasteless, and inodorous. It is the least refractive of all the gases. It has resisted every attempt to effect its liquefaction. It possesses magnetic properties analogous to, but much weaker than, those of iron. It is heavier than atmospheric air in the proportion of 1·1056 to 1·0000. It is very sparingly soluble in water, 100 volumes of which at ordinary temperatures can only retain about 3 volumes of the gas. Nearly all natural waters contain dissolved oxygen, and can only be freed therefrom by prolonged ebullition in vacuo. The chemical reactions of atmospheric air depend principally upon the oxygen which it contains; and, reserving the special chemistry of the atmosphere for consideration in a separate section, it will suffice for the present to regard the air which surrounds us as being, in its chemical relations, merely oxygen gas mixed, or diluted, with about four times its volume of an indifferent gaseous substance, nitrogen.

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(107) Oxygen in the free state, whether or not diluted with nitrogen, manifests considerable chemical activity, even at ordinary temperatures, but in a much less marked degree than the elements of the halogen family. With the single exception of fluorine, it has been made, directly or indirectly, to unite with every known element. Some oxygenous reactions are interesting from their employment as means for detecting the presence of the gas, or effecting its removal. Thus an alkaline solution of white indigo absorbs oxygen rapidly, at the same time becoming blue. An alkaline solution of a pyrogallate absorbs oxygen, forming an opaque black liquid. Nitric oxide gas, which is perfectly colourless, unites with oxygen to form deep orange-red vapours. Phosphorus slowly absorbs oxygen, as do also moist iron wire, moist lead-turnings, moist saw-dust, and many metallic compounds, such, for instance, as the ammonio-subchloride of copper, the prothydrates of iron and manganese, the white double cyanide of potassium and iron, &c.

The majority of the metals, when in the massive state, remain perfectly bright and unacted upon in dry oxygen or air; but in moist oxygen or air, many of them become slowly oxidised. The coating of oxide first formed frequently protects the metal from other than a superficial oxidisement, as is notably the case with lead. Some of the ordinarily permanent metals, when in a very finely divided state, for instance, lead as obtained by the ignition of its tartrate, and iron as produced by the ignition of Prussian blue, undergo so violent an oxidation, that spontaneous combustion results from their mere exposure to air or oxygen. Hence they are termed pyrophori. Various other bodies, which expose a large surface to the action of air or oxygen, become gradually heated through slow oxidation, and finally undergo spontaneous combustion. Greasy tow and woollen refuse are peculiarly liable to this action.

(108) Many substances, when heated to redness, unite with oxygen, and thereby give rise to the phenomena of combustion or burning. The combustions of phosphorus, charcoal, sulphur, iron, zinc, and naphthaline, in undiluted oxygen, constitute very brilliant experiments. In each case the results are oxidised compounds of the substance burned. It need scarcely be said that no loss of material occurs during the destruction of these substances by burning. The weight of oxidised products corresponds exactly with the weight of the body burned, plus the weight of the oxygen consumed. When an ordinary combustible body, such as wood, paper, or wax candle, is inflamed in air and then immersed in a vessel of oxygen, the combustion proceeds with greatly increased intensity. If the flame

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of the wood, paper, or wax candle be extinguished, and any portion of the substance be left in a glowing state, it will, when immersed in oxygen, immediately burst into flame. This is a very characteristic property of undiluted, or but slightly diluted, oxygen, which it shares only with nitrous oxide gas. A jet of hydrogen gas burns in oxygen as in air, but more rapidly. Of course the two gases can only unite where they are in contact with one another, that is immediately around the jet of hydrogen. Hence formerly the hydrogen was said to burn, and the oxygen merely to support combustion. But if a jet of oxygen be introduced into a vessel of hydrogen, the flame will proceed from the oxygen and the hydrogen become the supporter of combustion. For this purpose the hydrogen, contained in a large, somewhat narrow mouthed, inverted jar, should be ignited at the mouth of the jar. Then the jet of oxygen, in passing through the flame, will itself become ignited and burn in the atmosphere of hydrogen.

(109) The combustions which result from the union of oxygen with other substances are of great interest. Graham has well observed that "oxidation alone, of all chemical actions, is practised, not for the value of the products it affords, and indeed without reference to them, but for the sake of the incidental phenomena of combustion attending it." The chemical action exerted by different bodies upon one another is almost invariably accompanied with some alteration, usually an elevation, of temperature; and when this degree of temperature is so great as to be attended with an evolution of light, the phenomena of combustion are said to take place. The combustions due to the union of oxygen do not differ chemically from the combustions resulting from the union of other substances, but economically are of much greater importance, as furnishing our chief sources of artificial light and heat. We find that chemical action, of a sufficiently intense character to produce combustion, will frequently not take place without the aid of extraneous heat, but that the chemical action, when once set up, will evolve sufficient and more than sufficient heat to maintain the combustion. This is the case with our ordinary combustibles, such as coals, candles, and gas, which do not unite with oxygen at ordinary temperatures, but which, when once ignited, continue to burn. On the other hand, a mass of iron, such as a poker, when made red hot and exposed to the air, undergoes oxidation or combustion on its surface, but the quantity of heat, evolved by the superficial chemical action, is not enough to maintain the mass of metal in a state sufficiently heated to allow a

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continuance of the combustion taking place. But if the surface exposed to the chemical action of the air or oxygen be increased, and the mass of metal to be heated by the chemical action be decreased, then the combustion when once established will continue. In this way very fine iron wire may be burned, even in much diluted oxygen. The pyrophoric metallic iron, before alluded to, constitutes another illustration of the relations of surface and quantity as affecting combustion.

(110) The quantity of heat evolved during chemical action being definite in amount, and quite independent of the slowness or rapidity of the action, provided only that the same substances yield the same products, it follows, for instance, that the slow oxidation of iron in the air yields precisely the same quantity of heat as the rapid combustion of iron in oxygen gas; though the intensity of the heat, or the amount evolved within a given time and space, is very much less, and so in other cases of oxidation. The most important illustration of the production of heat by slow oxidation, or eremacausis, occurs in our own bodies. During the breathing of animals, fresh air or oxygen is taken into the lungs at each inspiration, and by its absorption thence into the general circulation, renders the blood of a bright scarlet colour. A portion of this absorbed oxygen oxidises the food and tissues, chiefly into water and carbonic acid, which are expelled during expiration, the blood by the loss of its free oxygen, or possibly by the production of carbonic acid within it, again becoming dark coloured. The quantity of heat generated during this process is found to be strictly proportionate to the quantity of oxygen consumed by the carbon, hydrogen, sulphur, &c., of the body.

(111) Oxygen is capable, directly or indirectly, of replacing hydrogen and chlorine; but one atom, or proportion, of oxygen is always the equivalent of two atoms, or proportions, of hydrogen and chlorine, as seen in the following equations which indicate respectively the conversion of alcohol into acetic acid by its direct oxidation, and of pentachloride of phosphorus into the oxichloride, or chloraldehyd, by its reaction with water: —

$$C_2H_4O_2 = C_2H_6O + O - H_2$$
$$P\,Cl_3O = P\,Cl_5 + O - Cl_2$$

(112) Oxygen (*ὀξὺς γεννάω*) was first so called by Lavoisier on account of its acidifying properties. At that time it was thought that oxygen was essential to the constitution of an acid, and that its principal action was to acidify. Davy first disproved

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this view by showing that chlorhydric acid contained no oxygen, and that alkalies as well as acids resulted from oxidation. Despite these facts, however, and although it now retains its name chiefly from habit, oxygen must yet be regarded essentially as the acidifier. An acid is merely a hydrogenised body, which can readily exchange its hydrogen for metal; and in bodies containing several atoms of hydrogen, we generally find the number of these that can be replaced by metal to be proportionate to the degree of oxidation of the compound. Thus, of the three bodies

1. H_3PO_2 Hypophosphorous acid,
2. H_3PO_3 Phosphorous acid,
3. H_3PO_4 Phosphoric acid,

the first can exchange but one, the second but two, and the third all three atoms of hydrogen for an equal number of atoms of protequivalent metal. Again, of the two bodies

1. $C_7H_6O_2$ Benzoic acid,
2. $C_7H_6O_3$ Salicylic acid,

the first can exchange but one, the second two atoms of hydrogen for metal.

Ozone.

(113) Under certain circumstances, oxygen gas acquires a greatly increased chemical activity, together with a peculiar smell. In this state it constitutes ozone (ὄζειν), and has the characteristic property of decomposing iodide of potassium with liberation of iodine. Oxygen gas through which electric sparks have been passed, that in which phosphorus, ether, turpentine, and some other substances have been slowly oxidising, and that produced by the electrolysis of an acid liquid, alike react with iodide of potassium as above described. According to Andrews, the ozone produced by these three processes is the same, and consists solely of oxygen in an allotropic state. According to Williamson and Baumert, the ozone produced by electrolysis is a teroxide of hydrogen H_2O_3, as is probably also that produced by the oxidation of phosphorus. With regard to the ozone produced by electrical discharges, they admit that perfectly dry oxygen is capable of being modified by such discharges, but consider that the peculiar properties of ozone are not manifested until the action of moisture upon the modified oxygen has resulted in the formation of teroxide of hydrogen. The recent conjoint experiments of Andrews and Tait, however, seem to have established the correctness of the former view.

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More than half a century after Van Marum's original observation, that oxygen through which electric sparks had been passed acquired a peculiar smell and a power of attacking mercury, Schönbein, in 1840, published his first paper on ozone. He showed that in the electrolysis of acidulated water, an odorous gas was produced at the positive pole, which might be preserved for a long time in well closed vessels. He also observed the same product to result from the discharges in air of a common electrical machine, and recognised the identity of the smell with that accompanying a flash of lightning. Soon after he noticed the production of ozone by the slow oxidation of phosphorus in moist air or oxygen. Marignac and De la Rive then showed that ozone might be obtained by passing electrical sparks through perfectly dry oxygen, a result confirmed by Frémy and Becquerel, and subsequently by Andrews. But they found, on the other hand, that dry air or oxygen did not become ozonised by its transmission over dry phosphorus. Frémy and Becquerel ascertained that pure oxygen gas, standing over a solution of iodide of potassium, might be completely absorbed by the passage of electric sparks through it. Dry oxygen, however, as shown by Andrews, can be only partially ozonised by electrical discharges; unless, indeed, the ozone be absorbed as fast as it is produced. Houzeau noticed the ozonic character of oxygen set free by the action of sulphuric acid upon peroxide of barium. According to De Luca, the oxygen evolved by the action of light upon plants is also ozonic.

(114) Ozone is best prepared by one or other of the following processes. *a.* Ozonised air or oxygen may be obtained by placing one or two sticks of clean moist phosphorus in a bottle of air or oxygen, when, after an hour or so, the smell of ozone will be very obvious. The sticks of phosphorus should then be taken out, and the gas washed with water to remove the phosphorous acid. If the phosphorus be allowed to remain in the bottle for several hours, the ozone gradually disappears. Or, a current of moist air may be slowly forced through a succession of large Wolfe's bottles, containing each a few sticks of clean phosphorus, and finally through a U-tube containing water or dilute alkali. The junctions should be as few as possible, and should be effected with sound corks, or preferably by grinding. Ozone may be at once produced by plunging a heated glass rod into a mixture of air and ether-vapour.

β. By electrolysis of water acidulated with sulphuric acid. According to Andrews, a mixture of one volume of sulphuric acid with three volumes of water is most productive; while Baumert recommends the

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electrolyte to consist of water strongly acidulated with both chromic and sulphuric acids. The following arrangement may be advantageously adopted. A coated wire, having attached to its extremity a piece of crumpled platinum foil, which constitutes the positive electrode, is dipped into the electrolyte contained in a cylindrical porous cell, and an inverted tube-funnel, just sufficiently small to slide into the cell, is suspended therein, over the foil. This funnel serves to collect the oxygen which, during the electrolysis, issues in a continuous stream from its narrow orifice. The negative electrode may be constituted of a plate of platinum foil dipping into another vessel of the electrolyte, surrounding the porous cell. Electrolytic oxygen has not been found to contain more than $\frac{1}{250}$ part of its weight of ozone, or rather of active oxygen.

γ. Ozone may be obtained by passing electrical discharges through air or oxygen. Oxygen gas, prepared by heating chlorate of potassium, is conducted successively through a strong solution of caustic potash, and over pumice and oil of vitriol. Electrical discharges may then be passed through the gas in its transit, whereby a stream of pure ozonised oxygen is obtained, or the gas may first be collected by displacement in suitable tubes, and be then ozonified by the discharge. Andrews is accustomed to collect his oxygen in a straight glass tube, one end of which, previously contracted by the blowpipe, is in communication with the supply of gas, while the other end is fused to an almost capillary piece of tubing, bent in the form of a U-gauge. After the tube has been two or three times alternately exhausted by an air-pump, and filled with oxygen, the extremity of the capillary gauge is detached from the air-pump, during the passage of the gas, and dipped into oil of vitriol. The supply of gas is continued for some time longer, and the excess allowed to bubble through the oil of vitriol in its escape. The contracted extremity of the reservoir part of the tube, in communication with the source of oxygen, is then sealed by the blowpipe, and a few bubbles of gas expelled by gentle warming. Upon cooling, oil of vitriol is drawn into the gauge, so as to confine the oxygen in the reservoir. The free extremity of the gauge is next sealed in such a manner as to leave a small space of air above the oil of vitriol. Then by means of platinum wires, previously fused into the reservoir, electrical discharges are passed through the oxygen, whereby it becomes ozonified. In this way, any alteration in the bulk or tension of the oxygen, consequent upon the production or subsequent destruction of the ozone, is recognisable by an alteration in the level of the oil of vitriol in

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the gauge. Andrews found that the Rühmkorff spark was ill suited for the production of ozone, and that even the ordinary machine spark was much less effective than the silent discharge, obtained by attaching one of the platinum wires of the reservoir-tube to the prime conductor, and the other to the ground, and turning the machine slowly.

(115) In addition to its property of displacing iodine from iodide of potassium, ozone is found to be rapidly absorbed by mercury, and to be completely destroyed or decomposed at a temperature of 250—300°. Availing himself of these properties, Andrews obtained the following results. When the silent discharge was passed through pure dry oxygen contained in one of his gauge tubes, condensation was observed to take place, at first rapidly and then more slowly. The maximum contraction ever obtained was equal to $\frac{1}{12}$ of the entire volume of the gas. On heating the contracted or ozonised gas to 300°, it recovered its original volume; and this alternate contraction by the silent discharge, and restoration by a temporary heat, could be repeated an indefinite number of times. The extreme contraction gradually diminished when the tube was set aside for some days. The ordinary electrical spark effected a very small contraction of the gas, not exceeding $\frac{1}{100}$ of the whole; and when the spark discharge was passed through the the gas contracted by the silent discharge, an expansion took place corresponding to the excess of contraction effected by the silent discharge, beyond that which the spark discharge could have produced. By introducing into the reservoirs of his tubes, before filling them with oxygen, small quantities of mercury or solution of iodide of potassium, contained in thin glass bulbs, and then ozonifying by the silent discharge, so as to produce a much contracted gas, Andrews was able to act upon the ozone with these reagents, which could be set free for the purpose by a smart concussion, and consequent fracture, of their containing bulbs. After the action of the mercury or iodide of potassium upon the contracted gas, it no longer underwent any permanent expansion when heated to 300°, showing the complete absorption or decomposition of the ozone by the reagent. But very curiously, this absorption of the ozone was not attended with any diminution in the bulk of the contracted oxygen. In other words, the active oxygen, absorbed by the reagent, occupied no part of the bulk of the ozonised gas, inasmuch as its removal did not diminish that bulk. When the ozone was absorbed by solution of iodide of potassium, the amount of iodine liberated was found to correspond exactly with the amount of

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original contraction, that is, with the quantity of oxygen which had apparently ceased to occupy space. The above remarkable result seems to be best explained by the following hypothesis. If we consider ozone to be a compound of oxygen with oxygen, and the contraction to be consequent upon their combination, then if one portion of this combined or contracted oxygen were absorbed by the reagent, the other portion would be set free, and by its liberation might expand to the volume of the whole. Thus, if we suppose three volumes of oxygen to be condensed by their mutual combination into two volumes, then on absorbing one-third of this combined oxygen by mercury, the remaining two-thirds would be set free, and consequently expand to their normal bulk, or two volumes :—

$$\underset{\text{2 Vols.}}{-\,+\,-}\quad +\quad \underset{}{+\quad -}\quad \underset{\text{2 Vols.}}{+\,-}$$
$$O\ O\ O\ +\ Hg_2\ =\ Hg_2\ O\ +\ O\ O$$

Upon this hypothesis, Andrews' maximum contraction of $\frac{1}{12}$ would indicate the conversion of $\frac{1}{4}$ of his oxygen into ozone.

Andrews also ascertained that a stream of dried electrolytic ozone, when heated to decomposition, and passed over phosphoric anhydride, did not afford a trace of moisture. When passed consecutively through solutions of iodide of potassium and oil of vitriol, the increase in the weight of the two liquids, from the absorption of the active oxygen, corresponded exactly with the equivalent of iodine set free, as estimated by Bunsen's volumetric method. According to Williamson and Baumert, however, dried electrolytic ozone does yield water as a product of its decomposition by heat. According to Baumert, also, dried electrolytic ozone when passed consecutively through solution of iodide of potassium and oil of vitriol, sets free a quantity of iodine corresponding to only $\frac{32}{50}$ of the total increase of weight of the two liquids. Hence the formula, previously suggested by Williamson, H_2O_3, for $H_2O_3 = H_2O + O_2$, or $50 = 18 + 32$, whence $O_2 = \frac{32}{50}$ of H_2O_3. Andrews found that electrolytic ozonised oxygen, when decomposed by heat in one of his gauge tubes, underwent a variable increase of bulk, according to the proportion of ozone present. The expansion, however, never exceeded $\frac{1}{250}$ of the entire volume of gas.

(116) The general characters of ozone are those of an oxidising agent. Thus, it corrodes organic matter, as shown by its rapid action on caoutchouc or vulcanite connecters. It bleaches most vegetable colours, as exemplified particularly by its conversion of indigo into isatin. It oxidates black sulphide of lead into white sulphate of

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lead, changes the yellow ferrocyanide into the red ferridcyanide of potassium, and turns moist sulphate of manganese to a brown colour, from the formation of the hydrated peroxide. It is absorbed by moist iron, copper, mercury, and silver, with production of their respective oxides. Moist silver is even converted into the state of peroxide. Dry ozone is also readily absorbed by dry mercury and dry iodine.

In some cases, however, ozone acts as a deoxygenant. Thus it decomposes peroxide of hydrogen and peroxide of barium, with evolution of inactive oxygen, derived both from the ozone and the peroxide, as represented hypothetically by the following equation (vide par. 129):—

$$\overset{-}{O}\,\overset{+}{O}\,\overset{-}{O} + \overset{+}{H_2}\,\overset{-}{O}\,\overset{+}{O} = 2\,\overset{-}{O}\,\overset{+}{O} + \overset{+}{H_2}\,\overset{-}{O}.$$

Dry ozone is decomposed in unlimited quantity by the dry peroxides of manganese and lead, and by black oxide of copper, these oxides not undergoing any alteration of weight by the reaction. It is also decomposed to an unlimited extent by dry silver leaf or filings. These unlimited effects may be explained by the successive, or simultaneous, occurrence of oxidation and reduction. Thus dry silver leaf is at first obviously oxidised by ozone; and the oxide of silver so formed is then reduced, and so on consecutively.

Ozone is practically insoluble in water and acid solutions. When ozonised gas is passed through potash or soda, the first portions are absorbed, probably from the presence of some organic matter in the alkaline liquid, but after a little time, the ozone passes through apparently unaltered.

Schönbein regards ozone as permanently negative oxygen. He also believes in the existence of a permanently positive oxygen, or antozone, which at present is known only in combination; and considers that inactive oxygen is a product of the union of ozone and antozone $\overset{-}{O}\,\overset{+}{O}$ (vide par. 129).

Water. — Protoxide of Hydrogen.

Symbol, H_2O; *Proportional number*, 18; *Vapour density*, 9; *Atomic volume*, □□.

(117) Water is presented to us by nature in the solid, liquid, and gaseous states. Extensive plains of ice occupy the polar regions, and large masses of water, holding a greater or less amount of saline

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matter in solution, constitute the oceans, rivers, lakes, &c., of warm and temperate zones. Water exists in variable quantities in the atmosphere, either dissolved as invisible vapour, or deposited in the form of clouds. In temperate and even in many hot climates, the surface of the land is usually more or less moist; while several minerals which exist in the earth's crust contain water in a state of chemical combination. Moreover, water is essential to all animal and vegetable tissues when in a living condition: it constitutes seven-eighths of the entire human body.

The most variously contrived experiments all concur in showing that water is constituted thus: by measure, of one volume of oxygen and two volumes of hydrogen; by weight, of sixteen parts of oxygen and two parts of hydrogen, or 88·889 per cent. of the former, and 11·111 per cent. of the latter gas. The composition of water was first demonstrated by Cavendish in 1781. The simplest typical hydride with which chemists are acquainted is chlorhydric acid HCl, a compound we have already considered somewhat minutely: the next typical hydride is water H_2O, which we have now under consideration. It is observable that any definite volume of steam, or gaseous water, contains exactly twice as much hydrogen as the same volume of gaseous chlorhydric acid. The other two terms of our series of typical hydrides, namely, ammonia H_3N, and marsh gas H_4C, will be subsequently described. Water H_2O, is intermediate in composition and properties between chlorhydric acid HCl, and ammonia H_3N.

(118) The under described experiments illustrating the composition of water, a point of primary importance in chemical science, are selected from the almost infinite number of reactions which result in the decomposition or formation of that compound. The analytical experiments are not susceptible of such rigorous exactitude as are the synthetical.

a. When the vapour of water is passed over red hot iron turnings, contained in a tube of porcelain or iron, it undergoes decomposition. The hydrogen passes off in a free state, and may be collected in a receiver, while the oxygen unites with the metallic iron, to form black oxide of iron, a product which may also be obtained by heating iron in air or oxygen: $2H_2O + Fe_3 = Fe_3O_2 + H_4$. By weighing the amount of water decomposed and of oxide of iron formed, Lavoisier determined the composition of water by this process with very considerable accuracy.

β. When water is submitted to electrolysis, it breaks up into oxygen and hydrogen gases, which are liberated respectively at the

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positive and negative poles of the battery. The bulk of hydrogen produced is sensibly twice as great as that of oxygen: $H_2O = H_2 + O$. The water used in this experiment must not be absolutely pure, or it will not transmit the current; the addition of any acid or saline compound renders the decomposition easy.

γ. When a solid ball of platinum, made white hot in the flame of the oxyhydrogen blowpipe, is suddenly plunged into water, it effects a decomposition of the water into its constituent gases, which can be collected together in a tube receiver. An alkaline solution of a pyrogallate will absorb the oxygen and leave the hydrogen, the volume of which last gas will be found to be twice as great as that of the oxygen absorbed; or, in other words, the hydrogen will be found to constitute two-thirds of the original gaseous mixture.

δ. If a jet of pure hydrogen gas, thoroughly dried by means of pumice and oil of vitriol, be burnt under a cold bell-jar, the interior of the bell-jar will speedily be covered with moisture, and water will gradually trickle down its sides, as a product of the union of the hydrogen gas with the oxygen of the air. The experiment may be made more strikingly by burning a jet of dry hydrogen in a closed globe filled, and continuously supplied, with dry oxygen. In this manner a considerable quantity of water may be produced from the combination of the two gases.

ε. If a mixture of one volume of dry oxygen with two volumes of dry hydrogen, contained in an eudiometrical tube, be exploded by the electric spark, or be caused to unite by means of a ball of spongy platinum, the whole of the gas will disappear, being converted into water. If a definite measure of oxygen be mixed with several times its bulk of hydrogen, and the mixture be exploded, then three times the volume of the oxygen, or one measure of oxygen and two measures of hydrogen, will disappear, and the quantity of hydrogen in excess remain unacted upon. Again, if a measured quantity of hydrogen be mixed with an excess of oxygen, and the mixture be exploded, one third more gas will disappear than is due to the hydrogen; or, in other words, for every two volumes of hydrogen, one volume of oxygen will also disappear, and a residue of pure oxygen remain. In the original experiment of Cavendish, a strong pyriform exploder, provided with platinum wires and exhausted by the air-pump, was screwed on to an ordinary capped gas-jar containing a mixture of one volume of oxygen with two volumes of hydrogen. On turning the stop-cock, a portion of the mixed gases was admitted into the exhausted ex-

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ploder, and was then, after re-turning the stop-cock, inflamed by means of an electric spark, whereby a film of moisture became condensed upon the inner surface of the exploder. The process was repeated several times, until an obvious quantity of water had been produced. Now-a-days, in the beautiful instruments of Bunsen, Regnault, Frankland, and Williamson respectively, the volumetric synthesis of water may be made with absolute exactitude. Oxygen and hydrogen gases, when exploded together, will unite in only one proportion, namely, one volume of the former with two of the latter gas; and any excess of this proportion of either gas will remain unacted upon. Inasmuch as oxygen gas is sixteen times as heavy as hydrogen, we can, from the above volumetric results, deduce the composition of water by weight, namely, sixteen parts, or one atomic proportion of oxygen, united with two parts, or two atomic proportions of hydrogen.

ζ. The most accurate experiments upon the composition by weight of water were conducted by Dumas, who employed a process essentially the same as that previously used by Berzelius and Dulong. Hydrogen gas was passed over a weighed quantity of oxide of copper heated to dull redness. The hydrogen reacted with the oxide of copper to form water which passed over, and metallic copper which remained, thus: $Cu_2O + H_2 = H_2O + Cu_2$. The quantity of oxygen lost by the oxide of copper, and the quantity of water produced by its combination, were estimated by weighing. For every hundred grains of water produced, the oxide of copper was found to have lost 88·889 grains. Hence the centesimal composition of water is:

Hydrogen	11·111
Oxygen	88·889
Water	100·000

The ratio $\frac{11{\cdot}11}{88{\cdot}88}$, equal, of course, $\frac{2}{16}$, corresponds to the volumetric formula H_2O. The details of the experiment are as follows:— Hydrogen gas, generated in a large Wolfe's bottle from purified zinc and dilute sulphuric acid, is made to pass first through a U-tube containing acetate of lead, to absorb any sulphuretted hydrogen; then through a couple of U-tubes containing sulphate of silver, to absorb any phosphuretted or arseniuretted hydrogen, and any sulphuretted hydrogen that may have escaped the lead solution; then through two U-tubes containing caustic potash to absorb the carburetted compounds with which hydrogen is generally contaminated; and,

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lastly, through two other U-tubes filled with phosphoric anhydride, to remove every trace of humidity. The last of these U-tubes is put in communication with a globe or flask made of difficultly fusible glass, and furnished with two necks placed horizontally, one opposite the other. This globe, having been accurately weighed, is then charged with oxide of copper, and again weighed. One neck being attached to the last U-tube, the other dips into a second two-necked, but empty, flask, destined to receive the water produced in the experiment. To the free neck of the empty flask are attached a couple of U-tubes, containing respectively weighed quantities of chloride of calcium and oil of vitriol, to retain the aqueous vapour which the escaping hydrogen would otherwise carry away with it. After the entire apparatus has been filled with hydrogen gas, heat is applied to the oxide of copper. The reaction then commences, and is continued until the oxide is completely reduced. After cooling, the hydrogen apparatus, with all its U-tubes, save the last two, containing the phosphoric anhydride, is separated. By means of an aspirator, a current of air is then drawn successively through the above two drying tubes, the oxide of copper flask, the water flask, and the terminal chloride of calcium and oil of vitriol tubes, so as to replace the hydrogen contained in them by atmospheric air, and thereby restore them to the condition in which they were originally weighed. The oxide of copper flask is next weighed, to ascertain the quantity of oxygen lost by combining with hydrogen, and the water-flask, with its chloride of calcium and oil of vitriol tubes, also weighed, to ascertain the quantity of water produced by the oxygen yielded by the oxide of copper. In his experiments, Dumas produced many ounces of water by the union of hydrogen with oxygen, as above described.

(119) The circumstances under which oxygen and hydrogen unite with each other to form water are peculiar. At ordinary temperatures a mixture of the two gases undergoes no alteration even when exposed to direct sunlight. A sudden and violent compression has produced their combination with explosion; but a much greater degree of compression effected gradually has been found unavailing. Several substances which are in other respects of a very inert chemical nature, have the property of causing, by their mere presence, the union of oxygen and hydrogen gases. Perfectly clean platinum is the most active of these agents. The efficiency of the platinum seems to be proportionate to its amount of surface and to its temperature, which, when the mass of metal is small, becomes rapidly augmented by the heat evolved from the

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constantly accelerated combination of the gases. With thin platinum foil, or fine platinum wire, the action takes place for the most part quietly. With spongy platinum the action is at first silent, but the heat evolved by the combination of the gases speedily raises the temperature, and consequently the activity of the metal, until it becomes red hot, when it explodes the mixture. To prevent this explosion spongy platinum is usually made into balls with fine clay, or meerschaum, whereby its action is moderated considerably. Platinum black produces an instantaneous combination, accompanied with explosion. Finely divided iridium, palladium, gold, silver, and some other metals, also charcoal, pumice-stone, and even crushed glass, exert, especially at elevated temperatures, a catalytic action, apparently similar in kind to, though much less in degree than, that effected by platinum. This catalytic action is exerted upon other gaseous mixtures, as well as upon that of oxygen and hydrogen. Certain moist, or preferably wet, organic substances in a state of decomposition, decayed wood and peat-earth, for example, are said to have the property of causing the gradual combination of oxygen and hydrogen gases. From what we know of similar actions, it seems probable that the union of one portion of oxygen with the carbon of decaying organic matter, might induce in another portion of oxygen a capability of uniting directly with hydrogen.

The combination of oxygen and hydrogen may be instantaneously effected by a solid heated even to dull redness, by the electric spark, and by flame. This instantaneous combination, if the gases are in any considerable quantity, takes place with a loud explosion. When a lighted taper is applied to a bladder filled with oxygen and hydrogen, mixed in the proportion of one volume of the former to two of the latter gas, the report is very violent. The heat developed by the combination at first causes a great expansion of the resulting steam which, however, is so immediately condensed, that the noise consequent upon its sudden expansion, and that consequent upon its sudden condensation, are apparently simultaneous. The ignition of five volumes of air mixed with two volumes of hydrogen, also produces a powerful explosion; but if either gas greatly exceeds that proportion, the mixture does not burn at all, or burns quietly with flame. An issuing jet of oxygen and hydrogen gases, mixed in the proportion to form water, burns with a pale blue, scarcely visible flame, but with an enormous evolution of heat. Of all substances in nature, oxygen and hydrogen gases produce by their combustion the greatest

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quantity of heat. This heat is rendered available by means of an instrument known as the oxyhydrogen blowpipe, which in its most powerful form consists of a strong metallic vessel or reservoir, into which the two gases, mixed in the proper proportions, are compressed by a condensing pump. This vessel is furnished with a stop-cock to regulate the exit of the gas, and attached thereto is a Hemming's safety-tube, which is usually separated by a second stop-cock from the terminal jet. The object of the safety-tube is to prevent any retrocession of the flame from the jet to the reservoir, an act that would inevitably lead to a most dangerous explosion. It consists of a strong brass tube, tightly rammed, by means of a conical wedge thrust into the midst, with fine brass wire, through the interstices of which the mixed gas issues. Now flame cannot exist, save at a very high temperature, and the cooling influence exerted by the great surface of good conducting metal, through which the flame would have to pass backwards, is sufficient at once to extinguish it in its retrograde movement. In other forms of the instrument the two gases are kept in separate reservoirs, usually constituted of waterproof bags, and are only allowed to mix at the base of a somewhat lengthened jet. On account of the oxyhydrogen flame usually burning in air, it is considered advisable by some manipulators to have the hydrogen somewhat in excess of the proportion requisite to unite with the pure oxygen. Moreover, the hydrogen may be replaced without any marked disadvantage by ordinary coal-gas. The oxyhydrogen blowpipe is capable of melting thick platinum wire, and of volatilising, or even boiling, metallic silver, the vapour of which takes fire, and burns with great brilliancy. Silica also can be reduced to the state of a viscid liquid similar to molten glass, and the stem of a clay tobacco pipe may be fused into an enamel-like mass. When an infusible solid, such, for instance, as lime, is heated in the flame of the oxyhydrogen blowpipe, it becomes intensely luminous. The light thus produced, known as the Drummond light, when reflected from a parabolic mirror in a pencil of parallel rays, has been recognised during daylight at a distance of 108 miles. In the improved form of this light, the lime is protected from crumbling by a cage of platinum wire, and is caused to rotate slowly by means of clock-work, so as constantly to expose a fresh surface to the flame.

(120) At ordinary temperatures, water is a transparent mobile liquid, tasteless, inodorous, and, save when in very large masses, colourless. Natural waters manifest every shade of brown, yellow,

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or green, from the presence of different contaminating substances, but the proper colour of water, when in a large body, seems to be a pure bright blue. Water is a perfectly elastic fluid, but the range of its elasticity is very limited. According to Regnault, it undergoes a compression of 47-millionths of its bulk for each pressure of an atmosphere. The density of water, at mean temperature in this country, at its point of maximum density on the continent (vide par. 121), is taken as the standard to which the specific gravities of liquids and solids are usually referred. A cubic inch of water at 60° Fahrenheit, weighs 252·456 grains. A cubic centimetre of water at 4° centigrade, weighs 1 gramme. Water at its point of maximum density is 770 times heavier than atmospheric air, at the temperature of zero, and under mean pressure. The great specific heat of water, already adverted to (vide par. 34), necessitates the addition or abstraction of a large quantity of heat in order to effect any change in its temperature. Hence masses of water in any situation constitute great equalisers of local temperature.

(121) At the temperature of zero*, water gradually solidifies into ice. The cooling of water is attended by a remarkable phenomenon which does not pertain to any other liquid. With each successive decrement of temperature it contracts regularly until cooled down to 4°, but every subsequent decrement of temperature beyond this point causes it to expand, and that to almost precisely the same extent as it previously contracted; so that if water at 4°†, its point of maximum density, as it is termed, be heated or cooled the same number of degrees, it will expand to exactly the same amount. The existence of this point of maximum density, although recognised for a long time previously, was first satisfactorily established by Hope, in the year 1804. He surrounded a deep cylinder of water at the temperature 10° by a narrow band of freezing mixture, and suspended in the water two thermometers, one at the top above the freezing mixture, and one at the bottom, below it. The deep thermometer soon indicated a lower temperature than the upper one, showing that the cooled water underwent contraction, and thereby becoming specifically heavier, occupied the bottom of the vessel. But at the temperature 4°, both thermometers became stationary for a time, and gave the same indication; after which, as the cooling went on, the upper thermometer was found to mark the lowest temperature, showing that the water cooled below 4° under-

* At 32° Fahrenheit.

† At 39·9° Fahrenheit.

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went expansion, and thereby becoming specifically lighter, occupied the top of the vessel. This property of water has a most important influence in the economy of nature. Water chilled at the surface by the winter's cold constantly descends in virtue of its contraction, and is replaced by warmer water until the temperature of the mass is diminished to 4°. After this point the cooled water no longer descends, but becoming lighter by each decrement of temperature, floats on the surface, and is there frozen. The ice thus formed increases slowly in thickness and in coldness, but it effectually prevents the transmission of cold to the water beneath, save to the layer in immediate contact with it, which, in consequence of its lightness, cannot descend to convey the cold downwards. As a result of this special arrangement, the temperature of any considerable body of water rarely descends below 4°, a degree of cold at which animal life can be readily sustained.

Water in cooling below 4° expands very gradually and very slightly, but at the temperature 0°, when it becomes ice, it expands suddenly, considerably, and with an enormous force, which even the strongest wrought-iron vessels cannot withstand. The specific gravity of ice, when compared with that of water at 4°, as unity, is 0·94: it seems to be a general, though not an invariable rule, that solid bodies are specifically lighter than the liquids from which they have congealed. Although at the temperature 0° water generally solidifies into ice, yet when exhausted of the air which it ordinarily contains, and kept perfectly quiet, it may be cooled down several degrees lower and still retain its liquidity. But on the least agitation, it, or a part of it, at once solidifies, and the temperature suddenly rises from — 10°, or even lower, to 0°. The freezing point of water is lowered by the presence of salts and other substances in solution. When a saline solution is exposed to a sufficient degree of cold, pure water crystallises out, while the salt remains dissolved in the mother liquor.

According to Provostaye and Dessains, the latent heat of water is 79°*, so that a pound of ice in becoming converted into water would reduce the temperature of a pound of water from 79° to 0°. Although, as we have said, water may be cooled below 0° without freezing, yet ice cannot be heated above 0° without melting. In consequence of the great latent heat of water, the temperature afforded by melting ice is in the highest degree constant and invariable, and hence is taken as one of the fixed points of temperature in every thermometric scale.

* The latent heat of water equals 142·2° Fahrenheit.

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Ice, despite the uniformity of its appearance, is a crystalline body, and is formed by the interlacement of crystals, which in running or turbid water, may often be obtained isolated from one another. They belong to the rhombohedral system, and occur in rhomboïds, short hexagonal prisons, and pyramidal dodecahedra. Snow generally presents itself in the form of triangular prisms arranged around a centre so as to form stars of great beauty and variety, but hexagonal plates, either simple or grouped together, may frequently be recognised. Hail also is sometimes obviously crystalline. Ice is colourless and transparent, a bad conductor of heat, and a non-conductor of electricity. At temperatures considerably below 0° it can be crushed to a dry non-adhesive powder, but at 0° it may after crushing be moulded together by an increased pressure into a transparent homogeneous solid. This adhesion of masses of moist ice or snow to one another is known as regelation.

(122) At the temperature of 100°, under a pressure of 760 millimetres, water boils and is converted into an invisible elastic fluid or vapour, occupying a volume 1696 times greater than that of the water from which it was generated.* The phenomenon of ebullition takes place only when the tension of the vapour or steam is equal to the pressure upon the liquid, in ordinary cases the atmospheric pressure. Now vapour-tension is dependent entirely upon temperature; and as a different pressure will require a different vapour tension to balance it, it follows that a difference in pressure will effect a corresponding difference in the ebullition-temperature, or boiling point.† Thus, under a pressure of two atmospheres, water

* Or at the temperature of 212° F., under a pressure of 29·92 inches.

† By the term "tension of vapour" is understood the amount of elastic force with which a vapour resists compression into the liquid state. Any attempt to compress a vapour at its maximum tension for the temperature into a less bulk, does not increase its tension as it would that of air or gas, but simply converts a portion of it into the liquid state, while the remainder of the vapour, provided its temperature is unchanged, will preserve the same tension as previously. Conversely, any attempt to decrease the tension of a vapour by affording it more space, merely causes the evaporation of a further quantity of liquid, and the production of an additional quantity of vapour having the same tension. But a vapour separated from the liquid that produced it, and at a pressure inferior to its maximum tension for the temperature, constitutes a gas, and its tension or elasticity, like that of any other gas, obeys the law of Boyle and Mariotte. Indeed our ordinary gases are merely the vapours of very volatile liquids existing at pressures inferior to their maximum tensions for the temperatures. Many of them, as we have already seen, may be condensed into the liquid state by increasing the pressure upon them above that of their maximum tension for the ordinary temperature; or by cooling them down, until their tension becomes inferior to the ordinary pressure; or by a combination of both methods.

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boils at 120·6°; that is to say, the tension or elastic force of watery vapour at that temperature is sufficient to balance the pressure of two atmospheres. On the other hand, in a good vacuum water will boil at the low temperature of 20°. At a degree of heat much below this, the appearance of ebullition is not manifested even in the most perfect vacua, notwithstanding that water has a measurable tension at the lowest temperatures to which it has been subjected.

Ebullition, or the formation of vapour beneath the surface, occurs only at a definite temperature determined by the pressure; but the quiet formation of vapour from the surface of water takes place at all temperatures, in proportion to the vapour-tension corresponding to the temperature. This evaporation proceeds in the air and gases generally as well as in a vacuum. The rapidity of the evaporation varies in an inverse ratio with the density of the air or gas, but the quantity of vapour eventually produced is practically the same as in a vacuum, and is dependent solely on the temperature. The ultimate tension of the vapour is scarcely affected, whether the space within which it is generated be vacuous or aerial. Thus, water admitted into a Torricellian vacuum at the temperature of 40° will at once depress the mercurial column 55 millimetres, or its tension will be measured by 55 millimetres; and when admitted into a confined bulk of dry air at the same temperature, it will gradually increase the tension of that air by 55 millimetres. In common with all definite chemical substances that are volatile, water has a fixed vapour-tension corresponding to every thermometric degree. The following table, on the authority of Regnault, gives the tension of the vapour of water at temperatures varying from — 30° to + 100°. The results in the first part of the table were obtained directly by passing water up into the vacuum of a barometer, and observing the extent to which the mercurial column was depressed at each particular temperature. The later results were obtained indirectly by establishing definite pressures with an exhausting pump, and then noticing the boiling point corresponding to each pressure; the boiling point of the water marking the degree of heat at which the tension of its vapour equalled the pressure upon its surface. The boiling point of water in this country may vary as much as three degrees Centigrade from differences in atmospheric pressure.

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Tension of Aqueous Vapour at Temperatures from — 30° to + 100°.

Temperatures in degrees C.	Tensions in millimetres.	Temperatures in degrees F.	Tensions in inches.
— 30°	0·365	— 22°	0·0144
— 25°	0·553	— 13°	0·0218
— 20°	0·841	— 4°	0·0331
— 15°	1·284	5°	0·0506
— 10°	1·963	14°	0·0818
— 5°	3·004	23°	0·1233
0°	4·600	32°	0·1811
5°	6·534	41°	0·2573
10°	9·165	50°	0·3608
15°	12·699	59°	0·5000
20°	17·391	68°	0·6847
25°	23·750	77°	0·9272
30°	31·548	86°	1·2421
35°	41·827	95°	1·6468
40°	54·906	104°	2·1616
45°	71·391	113°	2·8106
50°	91·982	122°	3·6213
55°	117·478	131°	4·6251
60°	148·791	140°	5·8583
65°	186·945	149°	7·3600
70°	233·093	158°	9·1769
75°	288·517	167°	11·3589
80°	354·643	176°	13·9623
85°	433·041	185°	17·0488
90°	525·450	194°	20·6870
95°	633·778	203°	24·9518
100°	760·000	212°	29·9220

While the pressure remains the same, no exacerbation of heat can increase the temperature of a liquid above its corresponding boiling point, but can only accelerate the formation of vapour having a tension equal to the pressure. But when water or other liquid is heated in a close vessel, the vapour constantly produced exerts a

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constantly increasing pressure upon the liquid, whereby its temperature and the consequent tension of its vapour are increased to an extent limited only by the strength of the vessel, which at a certain point will inevitably give way. Strong vessels arranged with suitable valves, to allow the safe heating of water to temperatures greatly above 100°, are used in the arts for generating high-pressure steam, and under the name of *digesters* for making extracts of animal and vegetable substances. The tension of watery vapour at temperatures above as well as below 100° has been ascertained by Regnault with great accuracy. The pressure was obtained by a forcing pump, and the boiling point corresponding to the pressure then observed. His results are shown in the accompanying table :—

Tension of Aqueous Vapour in Atmospheres from 100° to 230·9°.

Temperatures, C.	Atmospheres.	Temperatures. F.	Temperatures, C.	Atmospheres.	Temperatures, F.
100·0°	1	212·0°	198·8°	15	390·0°
120·6°	2	249·5°	201·9°	16	395·4°
133·9°	3	273·3°	204·9°	17	400·8°
144·0°	4	291·2°	207·7°	18	405·9°
152·2°	5	306·0°	210·4°	19	410·8°
159·2°	6	318·2°	213·0°	20	415·4°
165·3°	7	329·6°	215·5°	21	419·9°
170·8°	8	339·5°	217·9°	22	424·2°
175·8°	9	348·4°	220·3°	23	428·5°
180·3°	10	356·6°	222·5°	24	432·5°
184·5°	11	364·2°	224·7°	25	436·4°
188·4°	12	371·1°	226·8°	26	440·2°
192·1°	13	377·8°	228·9°	27	444·0°
195·5°	14	384·0°	230·9°	28	447·6°

The latent heat of steam, that is, the heat absorbed in the conversion of water at 100° into steam at 100°, is, according to Regnault, 537°*; or the heat required to vaporise 1 pound of boiling water will suffice to raise the temperature of 5·37 other

* The latent heat of steam equals 966·6 degrees Fahrenheit.

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pounds of water 100 degrees. Conversely, if the steam produced by the complete vaporisation of 1 pound of boiling water be condensed in 5·37 pounds of water at zero, there will result 6·37 pounds of water at 100°. The great latent heat of steam renders it invaluable in the arts as a means for conveying and imparting heat.

On account of its uniformity, the boiling point of water under mean pressure, 760 millimetres, has been taken as one of the standard points of temperature in every thermometric scale. Now, the regularity with which water boils, and the fixity of the temperature under a definite pressure, are largely dependent upon the great latent heat of steam. Vapours having a small latent heat are apt to be produced suddenly and explosively, while the liquids generating them undergo sensible, and even considerable, variations of temperature. In order for water to boil steadily at 100°, it should be heated in a metallic vessel, and should be pure, or free from saline matter. In glass vessels, water will frequently acquire a temperature of 101°, and boil irregularly, but the introduction of a coil of platinum wire will reduce the temperature to 100°, and render the ebullition uniform. In vessels lined with shell-lac the temperature of water will alternately rise as high as 105°, and, after each burst of vapour, sink down again to 100°. These irregularities are attributed to an adhesive action between the water and the vessel opposing the free development of vapour. The presence of a salt in solution heightens the boiling point of water. Thus a saturated solution of chloride of calcium boils at 179·5°. With the same saline solution, the elevation of the boiling point increases with the amount of salt dissolved; but the boiling points of different saline solutions are not comparable with one another according to any known law. Thus a saturated solution of nitrate of potassium, consisting of 100 parts water and 335 parts salt, boils at 116°; while a saturated solution of carbonate of potassium, consisting of 100 parts water and only 205 parts salt, boils at 135°. The steam evolved from these hot solutions immediately adjusts itself to the atmospheric pressure, and by its expansion sinks down to the temperature of 100°. The presence of air in water greatly facilitates ebullition. The minute ærial bubbles form so many atmospheres into which the steam can diffuse. Prolonged ebullition in vacuo is required to expel air completely from water in which it is dissolved, although by far the greater portion of it may be readily driven off. According to Donny, water deprived of air and heated in an open glass

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acquired a temperature of 182°, and then suddenly yielded an explosive burst of vapour, whereby the vessel was shattered into fragments.

(123) The decomposition of water into its constituent gases, by means of heat and electricity respectively, has been already referred to. Light is not known to exert any chemical action upon water, though Graham is inclined to regard the decomposition effected by white hot platinum as a result rather of light than heat. Water is decomposed by a great number of chemical substances, simple and compound. The members of the halogen family of elements abstract hydrogen and liberate oxygen. Thus, in the case of chlorine, we have the reaction $H_2O + Cl_2 = 2HCl + O$. Most other elements, that are known to decompose water, abstract oxygen and liberate hydrogen. The alkali- and alkaline earth metals effect this replacement of hydrogen at ordinary temperatures; magnesium requires a boiling temperature; while zinc, iron, uranium, &c., act only at a red heat. When steam is passed over red hot charcoal we have a similar decomposition, thus: $2H_2O + C = CO_2 + H_4$. Carbonic oxide CO, is always formed in addition, as a secondary result of the reduction of the carbonic anhydride CO_2, by the excess of charcoal. Phosphorus gradually decomposes water under the influence of light, and unites with each of its constituents to form phosphoric oxide and phosphuretted hydrogen. The most important decompositions resulting from the action of compound bodies upon water are those effected by chlorous and basylous oxides, whereby acid and basic hydrates are respectively produced. For instance, sulphuric anhydride SO_3, reacts with water H_2O, to form sulphuric acid H_2SO_4. Similarly caustic lime Ca_2O, reacts with water H_2O, to form two atoms of hydrate of calcium 2CaHO. Actions of this class are frequently very violent; thus sulphuric anhydride, when thrown into water, hisses like a red hot iron; and the slaking of lime is attended with a great rise of temperature. Although we are frequently able, by means of heat or other agencies, to expel the water of these hydrates and acids, and reproduce the oxides or anhydrides, yet there is no reason to believe that the water expelled pre-exists as such within the compounds. At the same time water is capable of attaching itself in atomic proportions to very many bodies, to form compounds in which it is believed to exist preformed in the state of water. Thus, sulphuric anhydride SO_3, unites with water H_2O, to form the compound H_2SO_4, as we have seen, but it can also unite with $2H_2O$ to form the compound $H_2SO_4.H_2O$, and with $3H_2O$ to form the compound $H_2SO_4.2H_2O$.

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Now it is found that sulphuric anhydride SO_3, and sulphuric acid H_2SO_4, differ chemically from one another in every important particular*; but the compounds H_2SO_4, $H_2SO_4.H_2O$, and $H_2SO_4.2H_2O$, correspond most exactly in their properties, and their few chemical differences are merely differences in degree, dependent on their different states of concentration. There are many cases, however, in which it is very difficult to decide whether the constituents of water form an integral part of the complex molecule, or whether they exist in the state of water superadded to the more simple molecule.

(124) When water attaches itself as an adjunct to solid bodies, it is spoken of as water of constitution or crystallisation. Crystallised salts in particular often contain a definite number of atoms of preformed water; and the same salt can frequently take up water in several different atomic proportions. Thus sulphate of calcium crystallises with two atoms of water, sulphate of copper with five, and the sulphates of magnesium, zinc, iron, &c., with seven. Sulphate of sodium crystallises with either ten or eight atoms of water, and phosphate of sodium with either twelve or seven. Borax crystallises from a hot concentrated solution in regular octahedra, containing five atoms of water; from a cooler and less concentrated solution in oblique rectangular prisms with ten atoms. As a general rule, the colder and more dilute the solution from which a salt crystallises, the greater the quantity of water taken up in the crystals. The different atoms of crystallisation-water in salts are retained with very different degrees of force. Thus crystallised sulphate of magnesium, dried in vacuo over oil of vitriol, retains two atoms of water. One of these may be got rid of by heating the salt to 132°, whereas a temperature of 210° and upwards is required to expel the other. Graham distinguishes this last atom of water in sulphate of magnesium, and the last one, two, or three atoms of water in several other salts, by the name of constitutional

* "The two bodies do not present any analogy; under no circumstances do they comport themselves in the same manner; their functions are entirely different. The first does not combine with metals; the second does, and at the same time liberates hydrogen. The first unites directly with metallic oxides; the second gives rise to double decomposition. The first does not decompose metallic chlorides, and even combines with some; whereas the second decomposes them. The first forms amides or amidic acids with the volatile alkaloids; the second gives rise to salts. The first behaves in one manner with alcohols, amides, and hydrocarbons; the second behaves in another. The parallel may be pursued as far as we please, and under no circumstance shall we discover any analogy between the reactions."—*Laurent's Méthode de Chimie.*

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water. This constitutional water may not unfrequently be replaced by basylous metallic oxides, so as to produce basic salts. Many salts, known as efflorescent salts, lose the whole or a part of their water of crystallisation by mere exposure to air at ordinary temperatures. Thus crystallised carbonate of sodium, exposed at a temperature not below 6° to a moderately dry atmosphere, loses five of its ten atoms of water, and crumbles into an opaque white powder. Under the same circumstances, crystallised sulphate of sodium loses the whole of its ten atoms of water. The more powerfully a salt retains its water of crystallisation the warmer and dryer must be the atmosphere which will cause it to effloresce: thus crystallised sulphate of copper remains unchanged in ordinary air, but effloresces readily in air that has been completely deprived of moisture. The efflorescence of a salt is facilitated not only by warmth and dryness, but by any condition which favours evaporation. Hence a salt effloresces rapidly in vacuo, especially when the watery vapour evolved is absorbed by some desiccating agent as fast as it is produced. Efflorescence is frequently promoted, or even determined, by a scratch or abrasion of the surface of a salt. According to Faraday, uninjured crystals of carbonate, phosphate, and even of sulphate of sodium, may be kept for years in an open dish without effloresing. It is found that salts give off their water most freely when in a finely pulverised state.

Under reversed conditions, salts and other compounds acquire their water of constitution or crystallisation, sometimes in a very striking manner. Plaster of Paris Ca_2SO_4, for instance, when mixed with water, forms a solid mass of hydrated sulphate of calcium or gypsum $Ca_2SO_4.2H_2O$. When anhydrous sulphate of copper is mixed with water, the penta-hydrated salt is at once produced, and the temperature rises to 135°. Ignited carbonate of sodium gradually recovers the whole of its ten atoms of water in a moist atmosphere. Many crystalline salts, whether or not hydrated, absorb water from the atmosphere in indefinite proportions, become damp, and eventually liquefy. Such salts, carbonate of potassium K_2CO_3, and chloride of calcium $CaCl.3H_2O$, for instance, are called deliquescent. Other bodies than salts act in a similar manner; thus sulphuric acid H_2SO_4, alcohol C_2H_6O, and hydrate of potassium KHO, absorb water with avidity. Deliquescent salts, and bodies having similar absorbent properties are often used as desiccating agents. Some desiccants, on the other hand, such as caustic lime Ca_2O, and phosphoric anhydride P_2O_5, undergo a definite chemical decomposition with the water they retain.

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Bodies having a marked tendency to absorb water are generally spoken of as hygroscopic.

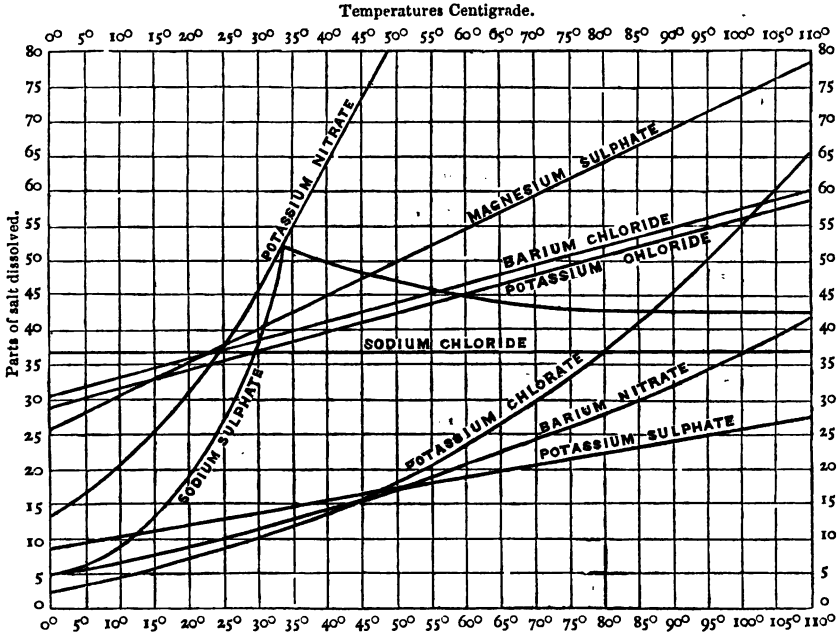
(125) Water has the property of dissolving many substances, solid, liquid, and gaseous. Alcohol and water mix with, or dissolve in, one another in all proportions. The solubility of some liquids, however, is limited, and that of others inappreciable. Thus, when ether and water are agitated together, a certain amount of solution takes place, but on subsidence the great mass of each liquid separates out, holding dissolved about one-tenth of its bulk of the other. Oil seems to be perfectly insoluble in water.

The proportion of any salt that can be dissolved in a given quantity of water is always limited, and, under fixed conditions, is special for each salt. Thus, water at mean temperature will dissolve $\frac{1}{700}$ of its weight of sulphate of calcium, and $\frac{2}{3}$ its weight of sulphate of magnesium. During the act of solution, the first portions of salt dissolve rapidly, the later portions more and more slowly, until complete saturation is attained. The saturating quantity of a salt does not bear any atomic relation to the quantity of solvent required, and is moreover variable under different conditions. Some salts, of which common salt is an example, dissolve in water to the same amount at every temperature. In most cases, the quantity of salt dissolved increases constantly with the temperature; and sometimes the increase is directly proportional to the temperature, or the same increment of salt is dissolved for every successive thermometric degree. Sulphate of potassium, sulphate of magnesium, chloride of potassium and chloride of barium afford examples of this behaviour. In the last two salts, the increments of solution for equal increments of temperature are the same. More frequently, however, the solubility of a salt increases in a greater ratio than the temperature: this is the case with chlorate of potassium, and with the nitrates of potassium and barium. Very rarely the solubility decreases as the temperature rises. This peculiarity is manifested by the hydrate, citrate, and butyrate of calcium, and by sulphate of cerium. Saturated solutions of these salts become turbid on heating, that of the butyrate of calcium almost solid. Still more rarely the solubility of a salt increases with the temperature up to a certain point, and then gradually decreases as the temperature continues to rise. Thus the proportion of sulphate of sodium that can dissolve in a given quantity of water increases rapidly with the temperature up to 33°, after which it abruptly begins to decrease, and continues gradually diminishing with each successive increment of temperature. But there is reason to believe

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that at 33° the salt undergoes a chemical change, that below that point we have the hydrated salt, above that point the anhydrous salt in solution.

Solubility of Salts in 100 *parts of Water.*



When two or more salts exist in solution together, they suffer mutual decomposition to a greater or less extent. Hence the laws of the solubility of mixed salts in water are somewhat complicated. A saturated solution of one salt can always take up some portion of another, and water can always dissolve a greater quantity of two or more mixed salts, which are not mutually precipitable, than of any one of them separately. The effect of variations in pressure upon the solubility of salts has not been investigated.

The solution of a solid or liquid in water is considered to depend upon an attractive or diffusive force exerted between the two bodies; and the resultant solvent action is said to differ from chemical action in the following particulars. Chemical combination occurs in definite proportions only, whereas solution takes place in indefinite proportions: thus water dissolves common salt in every possible proportion from the maximum downwards, while the solution of alcohol in water is absolutely unlimited. Again, chemical action

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is most marked between bodies of opposite characters, while solution is chiefly exerted between those which are more or less similar: thus metals dissolve in mercury, oxides and salts in water, fats and resins in oil, &c. Again, chemical action results in the production of bodies having properties entirely different from those of the reagents producing them, but in mere solution the properties of the reacting substances are retained to a greater or less extent: thus, syrup has the sweet taste of sugar, camphor-water the aromatic smell of camphor, litmus-infusion the purple colour of litmus, &c. Lastly, as pointed out by Gay-Lussac, the mere solution of a salt is attended with the production of cold, while the formation of a definite hydrate is attended with a development of heat, a circumstance which, according to Graham, "indicates an essential difference between solution and chemical combination." This production of cold, due only in part to the absorption of latent heat by liquefaction, is effected both by hydrated and anhydrous salts, provided the action is merely that of solution. Thus, hydrated sulphate of sodium $Na_2SO_4.10H_2O$, and anhydrous nitrate of potassium KNO_3, which last salt is not known in the hydrated state, alike produce a depression of temperature by their solution in water; but anhydrous sulphate of sodium, under the some circumstances, produces an elevation of temperature, due to the formation of the deca-hydrated salt, which then dissolves in the water as such.

From the above particulars it is evident that extreme cases of solution on the one hand, and of chemical action on the other, are readily distinguishable from one another. But there are many intermediate cases in which it is extremely difficult to draw the line; so that some chemists are inclined to regard solution and the allied class of phenomena as low forms of chemical action, or, at any rate, as transitional between purely chemical and merely mechanical action.

(126) All gases are soluble in water to a greater or less extent. The quantity of gas dissolved varies according to the nature of the gas, to the temperature, and to the pressure. Under fixed conditions, every gas has its specific coefficient of solubility, or absorption, not only in water but in other liquids. Thus at mean temperature and pressure, 100 measures of water dissolve 100 measures of carbonic anhydride, and only 2 measures of hydrogen. Again, 100 measures of alcohol will dissolve 288 measures, whereas the same bulk of water will dissolve only 16 measures, of olefiant gas. As a general rule, the quantity of gas absorbed by water or

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other liquid varies inversely as the temperature; but the diminution of solubility for an increase of temperature is special for each gas, and special for each temperature, according to no known law. In the less soluble gases, the variation of solubility at different temperatures is scarcely appreciable, and in the case of hydrogen appears to be absolutely *nil*. The solubility of different gases in water, at temperatures of 0° and 15°, and under a pressure of 760 millimetres, is shown in the accompanying table:—

Volumes of Gas absorbed by 100 *volumes of Water.*

Gases.	Vols. at 0° C.	Vols. at 15° C.
Hydrogen	1·93	1·93
Nitrogen	2·03	1·48
Atmospheric air	2·47	1·79
Ethyl	3·15	2·15
Carbonic oxide	3·28	2·43
Oxygen	4·11	2·99
Marsh gas	5·45	3·91
Methyl	8·71	5·08
Olefiant gas	25·63	16·15
Nitrous oxide	130·52	77·80
Carbonic anhydride	179·67	100·20
Chlorine	solid	236·80
Sulphydric acid	437·06	323·26
Sulphurous anhydride	6886·10	4356·40
Chlorhydric acid	50580·00	45780·00
Ammonia	114800·00	78270·00

By prolonged boiling, the less soluble gases may be completely expelled from water in which they are dissolved, but not the more soluble gases, with the exception of ammonia. Thus when water saturated with chlorhydric acid gas at the ordinary temperature is boiled under a pressure of 760 millimetres, the acid is at first evolved more rapidly than the water, until the temperature rises to 110°. At this point, the liquid in the retort and the distillate each contain 20 per cent. of chlorhydric acid, and this composition remains constant throughout the boiling. Conversely, a solution containing less than 20 per cent of chlorhydric acid becomes concentrated to that extent by boiling. According to Roscoe, the constant composition and boiling point of the acid does not depend upon the

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formation of a definite hydrate, but results from the establishment of a constant relation between the tensions of the aqueous vapour and of the gas. The value of this ratio between the tensions varies with the pressure, so that at every special pressure a diluted chlorhydric acid of special composition and of special boiling point distils over. Although the amount of gas that can be absorbed by water increases with the diminution of temperature, yet the less soluble gases are liberated completely during the act of freezing. The more soluble and liquefiable gases, however, such as ammonia and the chlorhydric, sulphurous, sulphydric, and carbonic acids, are not evolved but become frozen with the water.

The effect of pressure upon the solubility of gases was first aphorised by Henry in 1803, in the following proposition, now known as Henry's law of pressures. "Under equal circumstances of temperature water takes up, in all cases, the same volume of condensed gas, as of gas under ordinary pressure." So that water at 15°, for instance, dissolves its own volume of carbonic anhydride at every pressure; but inasmuch as the weight of gas in a given volume varies directly with the pressure, at twice the pressure twice the weight of carbonic anhydride is absorbed, and so on. Conversely, diminution of pressure produces an evolution of dissolved gas. Thus, when water saturated with any gas at ordinary pressure is placed under the air pump, the gas will escape as the air is rarefied. But it is not possible by mere rarefaction to expel the whole of the dissolved gases from water, more especially those which are freely soluble, on account of the production of that constant relation between their tensions and the tension of aqueous vapour, which has been already referred to. Aqueous chlorhydric acid, for instance, when placed under the exhausted receiver of an air pump, at first evolves chlorhydric gas, but at a certain dilution the acid and water distil over together. Dalton, in 1805, established a higher generalisation, now known as Dalton's law of partial pressures, which is as follows. In any mixture of gases, the proportion of each individual gas absorbed varies directly with the pressure exerted by that particular gas, or in other words, with its proportion present in the mixture.* Henry's law is obviously only

* One gas is to another as a vacuum; hence in any bulk of mixed gases, each individual gas is unaffected by the pressure of the others, and expands to fill the entire space as though it were actually vacuous, and exerts the pressure due to its elasticity in its expanded state; so that in atmospheric air, for instance, the $\frac{1}{5}$ of oxygen exerts only $\frac{1}{5}$ of an atmospheric pressure, while the $\frac{4}{5}$ of nitrogen exert $\frac{4}{5}$ of an atmospheric pressure.

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one special case of Dalton's, namely, that in which the volumes or pressures of certain gases are infinitely small as compared with the volume or pressure of the particular gas absorbed. It follows, as a consequence of Dalton's law, that when the volume of mixed gases is infinitely large as compared with the volume of water, the amount of each gas dissolved by the water will be the product of its coefficient of solubility into its proportion in the mixture; but in a limited bulk of mixed gases of unequal solubility, allowance must also be made for the alteration in the relative pressures effected by the unequal absorption. In the case of atmospheric air, however, the bulk of which is infinitely large, the calculation is as follows:—

	Coefficient at 15°.		Proportion in air.		Proportion dissolved.	
Oxygen	·0299	×	·2096	=	·00626	·01795
Nitrogen	·0148	×	·7904	=	·01169	

Now the ratio $\frac{626}{1169} = \frac{7}{13}$, so that rather more than one-third the bulk of air dissolved in water consists of oxygen. The nitrogen dissolved in water is said to be expelled by ebullition with greater facility than the oxygen.

It follows, as another consequence of Dalton's law, that when water saturated with one gas is brought into contact with another, the second gas, in proportion to its volume, will expel the first, and if its volume be infinitely great will expel it altogether. Thus, when a given quantity of water, saturated with marsh gas at mean pressure, is brought into contact with a limited bulk of air, the dissolved marsh gas being then subjected to no pressure, will escape into the space of air until the elastic pressure of the gas evolved balances the solubility of the gas retained. Simultaneously the air will be dissolved by the water until the quantity dissolved accords with the reduced elasticity of the remainder. If the bulk of air be infinitely great, the evolved marsh gas will never be able to exert any pressure upon itself, and will escape altogether. Hence it is impossible to keep a gas pure when standing over a liquid in which air is in any degree soluble. For, when a jar of marsh gas, for instance, is standing over water freely exposed to the air, the water absorbs the exterior air which it evolves into the limited atmosphere of marsh gas, and absorbs the marsh gas contained in the jar which it evolves into the exterior atmosphere, until the marsh gas is completely absorbed, and its place supplied with a volume of atmospheric air, much less, however, than the original volume of the marsh gas, on account of the inferior coefficient of solubility of atmospheric air.

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The accuracy of Dalton and Henry's law has been established with great exactitude by Bunsen, except in the case of those more soluble and condensable gases which do not rigidly obey Boyle's law of pressures. With regard to some of these, namely, ammonia, chlorhydric acid, sulphurous anhydride, and chlorine, Roscoe has shown that Dalton and Henry's law is not strictly applicable, save within comparatively narrow limits of both temperature and pressure. It seems probable, especially in the case of chlorine at low temperatures, that a tendency to produce definite chemical compounds may complicate the simpler results due to mere physical absorption. The absorption of the more soluble gases especially is attended with an evolution of heat. The bulk of liquid increases considerably, and its specific gravity, save in the case of ammonia, also increases in proportion to the amount of gas dissolved. Gaseous absorption, which is far from being an instantaneous process, is greatly facilitated by agitating the liquid and the gas with one another. Conversely, the liberation of dissolved gases by diminution of pressure is not by any means instantaneous, but is promoted by agitation, and by dropping porous or angular bodies into the liquid. Gases are much less soluble in saline solutions than in pure water. Hence the addition of soluble salts to water promotes the liberation of the dissolved gases.

(127) Water is not met with naturally in a state of absolute purity, but that produced by melting fresh water ice is often uncontaminated save with minute traces of ammonia and carbonic acid. Pure water is obtained by distillation. The portion that first comes over should be rejected, as liable to contain volatile impurities; a residual portion should not be driven over from the still, while the intermediate portion only should be collected for use. For special experiments, where absolute purity is required, this water should be twice redistilled: first, with phosphoric acid, to hold back any volatile alkali; and then with hydrate of potassium, or caustic lime, to hold back any volatile acid.

Rain water, collected in the neighbourhood of large towns, generally contains, in addition to nitrate and carbonate of ammonium, sulphate of ammonium, organic and carbonaceous matters, and, it is said, traces of fixed alkaline chlorides, derived from the combustion of fuel going on within the town. Even in country districts, the first rain that falls after a drought is contaminated with nitrate and carbonate of ammonium, and with organic matter, but the water of later rains is almost free from impurity. *River water* consists principally of rain water

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which, having fallen in more elevated districts, has gradually drained, over and through the soil, into lower districts, whence it travels downwards to the sea. The characters of river water are very variable, and depend chiefly upon the nature of the drainage area from which the river is supplied. Thames water, which is collected for the most part from an alluvial soil, contains about 18 grains of dissolved matter in a gallon, two-thirds of which consist of carbonate of calcium, the next most important constituents being sulphate of calcium and chloride of sodium. The Dee, of Aberdeen, which drains a granite district, contains in a gallon about 3 grains only of saline matter, consisting principally of carbonate of calcium, but also yielding marked quantities of potash-salts derived from the felspar of the granite. The Swansea rivers again, which drain a carboniferous district, abounding in pyrites, contain 3 grains and upwards per gallon of saline matter, consisting principally of sulphate of calcium. River water, in the neighbourhood of towns, is usually contaminated with sewage products from the artificial drainage of the towns.

Spring water is derived from rain water, which, having percolated the earth to a greater or less depth, is by natural or artificial means again brought to the surface. As a general rule, spring water contains a greater amount of dissolved matter than river water, on account of the greater quantity of earth that has been exposed to its solvent action. Rivers, however, occasionally take their origin in, or are largely contributed to by, springs. Spring water, also known as pump or well water, varies in composition according to the nature of the strata from which it is obtained. The spring waters of London are derived from three principal sources, namely, from shallow wells dug in the gravel above the London clay, from wells dug in the London clay, and from Artesian* wells dug, or rather bored, into the plastic clay, sand, or chalk, below the London clay. The shallow well-waters of London vary much in composition from one another, and from time to time. They yield from 20 to 120 grains of residue per gallon, and are liable to considerable contamination with sewer and cesspool products, as are indeed the shallow well-waters of towns generally. The water of the London clay is characterised by the abundant

* Artesian waters are properly those waters which rise spontaneously to the surface by hydrostatic pressure, on boring through the impervious strata by which they are confined into the porous strata in which they are collected; but the term Artesian is now generally applied to water yielded by deep wells constructed by boring, even when it has to be raised to the surface by pumping.

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presence therein of sulphate of calcium, the mineralogic name for one form of which is selenite, whence this water is called selenitic. The deep or Artesian well-water of London has a very constant composition, and is free, to a great extent, from organic impurity. It is characterised by a marked alkaline reaction, which is not affected by boiling, and depends upon the presence of a considerable amount of carbonate of sodium, derived probably from the action of rain water rich in carbonic acid, upon silicates of sodium existing in the strata overlying the chalk, in which the water principally collects. This water, which does not contain more than 3 or 4 grains of carbonate of calcium in a gallon, must not be confounded with the proper chalk-water yielded by chalk-springs in the neighbourhood of London, which is free from carbonate of sodium, and contains from 18 to 20 grains of carbonate of calcium in a gallon. *Lake water* corresponds in its characters with the river water of similar districts, lakes indeed being frequently mere expansions of, or reservoirs attached to, adjoining rivers. The supply, like that of river water, is derived chiefly from surface drainage, sometimes also from springs. Lakes are, for the most part, found in mountainous districts of the older formations, and the water of such lakes is very free from saline contamination. The Loch Katrine water now supplied to Glasgow contains only about $2\frac{1}{2}$ grains of saline matter in a gallon.

Domestic waters, whether obtained from rivers, springs, or lakes, are spoken of as hard or soft, according to the degree in which they possess the property of curdling soap. This curdling depends upon the formation of an insoluble compound, by the union of the fatty acids of the soap with the lime or magnesia of the hard waters. In order to estimate the hardness of waters, Dr Clark employs a standard solution of soap in alcohol, which he adds gradually from a burette to a thousand grain-measures of the water under examination, until no further curdling takes place, and a permanent lather is obtained. The quantity of soap required to produce this lather indicates the hardness of the water. The standard solution is made of such a strength that a degree of hardness corresponds with the curdling effect produced by the solution of a grain of carbonate of calcium in a gallon of water. The hardness dependent upon the presence of sulphate of calcium may be removed by the addition of carbonate of sodium to water; while that dependent upon the presence of acid carbonate of calcium may be removed by boiling, or by the

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addition of lime-water. Either one of these processes effects a separation of the dissolved lime-salt by precipitating neutral carbonate of calcium.

Sea water has altogether a very uniform composition, although indeed the amounts of saline matter yielded by different seas are not precisely the same. Sea water has a specific gravity of about 1027, and contains on the average some 2500 grains of dissolved matter in a gallon, including about 1900 grains of common salt, and 400 grains of chloride and sulphate of magnesium. The quantity of salts in sea water is continually increasing; for the pure water, always evaporating or distilling from the sea, supplies the rain-fall of the earth's surface, and this, after scouring the soil over or through which it flows, returns to the sea in the form of rivers charged with saline impurity. Hence the sea becomes the recipient of all soluble matters washed from the earth's crust.

Mineral waters contain either some unusual constituent of water, or a great excess of some ordinary constituent. The temperature of such waters is for the most part constant, and in some, known as thermal waters, is very considerably above that of the atmosphere. The principal varieties of mineral waters are the chalybeate or ferruginous, the sulphuretted or hepatic, and the saline. Chalybeate waters are either carbonated as that of Tunbridge wells, or sulphated as that of the Isle of Wight, which contains sulphate of aluminum in addition to sulphate of iron. Hepatic waters are characterised by the presence of sulphuretted hydrogen, which is the cause of their offensive smell. The chief British hepatic springs are those of Harrogate, in England, and Moffat in Scotland. Saline waters are of several kinds. Thus we have purging springs, containing considerable quantities of either sulphate of sodium or sulphate of magnesium. The former salt prevails in the waters of Leamington and Cheltenham, the latter in the waters of Scarborough, whence their bitterness. Brine springs, containing chloride of sodium as the principal constituent, are found chiefly in Nantwich and Droitwich, in England, but some of the Cheltenham and Leamington springs are also very rich in common salt. Calcareous waters, characterised by the presence of chloride, sulphate, and carbonate of calcium, are exemplified by the waters of Bath, Buxton, and Bristol, the springs of which places are for the most part thermal. Alkaline waters contain carbonate of sodium as their chief constituent, and are usually effervescent from the presence of carbonic acid. The Selters and Vichy waters belong to this class, but no good examples are

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found in England. The Geyser springs of Iceland are characterised by the large quantity of silica they contain, amounting to one half the total residue they yield on evaporation.

Peroxide of Hydrogen.

Symbol H_2O_2; *Proportional number* 34.

(128) This interesting compound was discovered by Thenard in 1818. *a.* It is made by the action of an acid, usually chlorhydric acid, upon hydrated peroxide of barium, according to the equation,

$$2HCl + Ba_2O_2 = 2BaCl + H_2O_2.$$

It is necessary for its successful preparation that the peroxide of barium employed should be free from heavy metallic oxides, and particularly from those of manganese and iron. A known quantity of chlorhydric acid, diluted with eight or ten times its volume of water, is placed in a beaker surrounded with ice or a freezing mixture. A quantity of peroxide of barium, rather less than sufficient to neutralise the acid, is then ground to a fine paste with water, and added little by little to the acid, in which it should dissolve without effervescence. Diluted sulphuric acid is next added cautiously, in order to precipitate the dissolved barium as sulphate, and reproduce chlorhydric acid to act upon a fresh quantity of peroxide: —

$$H_2SO_4 + 2BaCl = Ba_2SO_4 + 2HCl.$$

The liquid having been filtered from the insoluble sulphate of barium, a second proportion of the peroxide of barium paste is added gradually as before. This treatment of precipitation with sulphuric acid, filtration, and addition of peroxide, is repeated several times. After the sixth or seventh addition, when the liquid has become sufficiently charged with peroxide of hydrogen, sulphate of silver is added, at first freely, at last very carefully, so as exactly to precipitate, in the form of chloride of silver, the whole of the chlorine both of the chloride of barium and the chlorhydric acid: —

$$Ag_2SO_4 + 2BaCl = Ba_2SO_4 + 2AgCl.$$
$$Ag_2SO_4 + 2H\,Cl = H_2\,SO_4 + 2AgCl.$$

After filtration, the sulphuric acid set free from the sulphate of silver, is exactly neutralised, at first with a paste and afterwards

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with a solution of hydrate of barium. The sulphate of barium thus produced, having been separated by filtration, the clear liquid, consisting only of an aqueous solution of peroxide of hydrogen, is placed in a dish and evaporated in vacuo over oil of vitriol. The water evaporates much more rapidly than the peroxide of hydrogen, the greater part of which is eventually left in a concentrated or dehydrated state. The peroxide itself volatilises slowly, and consequently must not be left too long under the exhausted receiver, lest it should disappear entirely.

β. Pelouze abridges the above process considerably by adding the paste of peroxide of barium to a solution of fluosilicic, instead of chlorhydric, acid. The resulting peroxide of hydrogen solution is then filtered off from the insoluble fluosilicate of barium, and concentrated by evaporation in vacuo over oil of vitriol. Most of the reactions of peroxide of hydrogen may be obtained with its unconcentrated aqueous solution, or even with the original solution of peroxide of barium in chlorhydric acid.

(129) Peroxide of hydrogen is a colourless, transparent, somewhat syrupy liquid, of sp. gr. 1·452, which does not solidify at $-30°$. It evaporates slowly in vacuo without decomposition. It speedily bleaches litmus and other vegetable colours without first reddening them. It has a styptic metallic taste, and corrodes the skin and mucous membrane, with the formation of white eschars. It is a very unstable compound, and by mere contact with certain substances, or spontaneously, or by a slight elevation of temperature, undergoes decomposition into water and oxygen. The decomposition of the moderately concentrated peroxide is not unfrequently attended with explosion, always with a development of heat, sometimes with a development of light in addition. The oxygen given off by heating a weighed portion of the peroxide, diluted with water to moderate the reaction, may be collected in a volumeter over mercury, and from its amount the composition of the peroxide can be deduced.

As might be expected, the solution of peroxide of hydrogen is a powerful oxidating agent. It converts arsenious acid into arsenic acid, sulphurous acid into sulphuric acid, sulphide of lead into sulphate of lead, and the hydrated protoxides of manganese, iron and cobalt, into the peroxide and sesquioxides respectively. The prothydrates of barium, strontium, and calcium are transformed into their corresponding peroxides which, being insoluble, are precipitated. The concentrated solution of peroxide of hydrogen acts with great violence upon certain of the elements,

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selenium, arsenic, molybdenum, chromium, &c., converting them at once into their highest oxides.

Certain bodies, among which are included charcoal, many metals, and some metallic oxides, induce by their mere contact a more or less violent decomposition of the peroxide into water and oxygen, without themselves undergoing any change: gold, platinum, and silver, particularly when in the precipitated or spongy state, act most violently, and cause a great disengagement of heat. A slightly acid solution of the peroxide is less amenable to the action of these agents than is the pure aqueous solution; alkalies on the other hand facilitate the decomposition. The action of the above-mentioned bodies in causing the decomposition of the peroxide is termed catalytic. Its nature, however, is not at present understood (vide par. 116).

But the most remarkable circumstance connected with peroxide of hydrogen is its property of acting as a reducing agent. When peroxide of hydrogen, or its analogue peroxide of barium, is added to any one of the following substances, namely, the protoxides of silver or mercury, the peroxides of manganese or lead, the chromic, permanganic, and ferricyanic acids or their salts, not only is oxygen evolved from the peroxide of hydrogen, but also from the other oxidised body. Several of these reactions were noticed by Thenard in 1818, but they were first minutely examined and explained by Brodie in 1850. In accordance with his views, it seems that the second atom of oxygen in the peroxides of hydrogen and barium is not merely retained in an unstable state of combination, but that it is, by association with the oxide of an electro-positive element, like hydrogen or barium, thrown into a polar state, opposite to the polar state of the oxygen in unstable protoxides, and to that of the loosely combined oxygen in the more or less chlorous peroxides. Hence when the peroxide of hydrogen or barium is brought into relation with one or other of these oxygenised compounds, the two oppositely polarised oxygens unite with one another as indicated in the following formulæ:—

1. $\overset{+}{Mn_2}\overset{-}{O}\overset{-}{O} + \overset{+}{H_2}\overset{-}{O}\overset{+}{O} = \overset{+}{Mn_2}\overset{-}{O} + \overset{+}{H_2}\overset{-}{O} + \overset{+}{O}\overset{-}{O}$

2. $\overset{+}{Ag}\overset{-}{Ag}\overset{-}{O} + \overset{+}{H_2}\overset{-}{O}\overset{+}{O} = \overset{+}{Ag}\overset{-}{Ag} + \overset{+}{H_2}\overset{-}{O} + \overset{+}{O}\overset{-}{O}$

3. $\overset{+}{Cr_4}\overset{-}{O_3}\overset{-}{O_3} + \overset{+}{H_6}\overset{-}{O_3}\overset{+}{O_3} = \overset{+}{Cr_4}\overset{-}{O_3} + 3\overset{+}{H_2}\overset{-}{O} + 3\overset{+}{O}\overset{-}{O}$

4. $\overset{-}{I_2} + \overset{+}{H_2}\overset{-}{O}\overset{+}{O} = 2\overset{+}{H}\overset{-}{I} + \overset{+}{O}\overset{-}{O}$

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Brodie has shown that, in the third and fourth reactions, the amounts of oxygen set free correspond exactly with the above expressions. In the other two reactions, some additional oxygen is set free catalytically from the decomposition of the peroxide *per se*. For finely divided metallic silver has the property of decomposing peroxide of hydrogen catalytically, whence the oxygen liberated from the oxide of silver, according to the second equation has not been made to constitute more than 49, instead of 50, per cent. of the total quantity of oxygen evolved. It is observable that, in no case, can the oxygen from the peroxide constitute less than one-half of the total oxygen liberated. The above reactions are perfectly comparable with admitted reactions showing the formation of hydrogen and the radicles, for example:—

$$\overset{+}{Cu}_2\overset{-}{H} + \overset{+}{H}\overset{-}{Cl} = \overset{+}{Cu}_2\overset{-}{Cl} + \overset{+}{H}\overset{-}{H}.$$

$$\overset{+}{Zn}(\overset{-}{C_2H_5}) + (\overset{+}{C_2H_5})\overset{-}{I} = \overset{+}{Zn}\overset{-}{I} + (\overset{+}{C_2H_5})(\overset{-}{C_2H_5}).$$

Schönbein, apparently unaware of Brodie's researches, has recently drawn attention to the phenomena of deoxidation effected by the peroxides of hydrogen and barium, and has shown that ozone is rendered inactive by them. He regards ozone as permanently negative oxygen, $\overset{-}{O}$, which can form ozonides of silver, of manganous oxide, &c., and which, in the above reaction, is neutralised by the permanently positive oxygen or antozone, $\overset{+}{O}$, of the peroxide of hydrogen; whereas, according to Brodie, the polarity of the oxygen depends upon the nature of the body with which it is associated, and is manifested only at the instant of its dissociation.

Schönbein has confirmed the observations of Meidinger and others, that peroxide of hydrogen may sometimes be detected in water which has undergone electrolysis. He seems also to have shown that traces of peroxide of hydrogen are produced in many cases of slow oxidation occurring in the presence of moisture, for example, those of phosphorus, ether, zinc, &c. This production of peroxide of hydrogen he considers to be correlative of the other oxidation. Thus when moist zinc-filings are oxidised by exposure to air, a quantity of peroxide of hydrogen, which may be dissolved out by water and submitted to chemical tests, is formed according to the following equation:—

$$\overset{+}{Zn}_2 + \overset{+}{H}_2\overset{-}{O} + \overset{+}{H}_2\overset{-}{O} + \overset{+}{O}\overset{-}{O} = \overset{+}{Zn}\overset{+}{H}\overset{-}{O} + \overset{+}{Zn}\overset{+}{H}\overset{-}{O} + \overset{+}{H}_2\overset{-}{O}\overset{+}{O}.$$

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Peroxide of hydrogen, even in a very dilute state, may be recognised either by its oxidising or reducing properties. Thus it decolorises a solution of indigo, especially in the presence of sulphate of iron, which apparently serves to convey the oxygen from the peroxide to the indigo; and similarly it liberates iodine from a solution of iodide of potassium, starch, and sulphate of iron. On the other hand, it decolorises a solution of permanganate of potassium, by reduction; and causes a blue precipitate in a solution containing perchloride of iron and ferricyanide of potassium. It eventually reduces chromic acid to the state of chromic hydrate, but its first action is to produce, by oxidation, a very unstable perchromic acid. This compound, which has a deep blue colour, is readily soluble in ether, and its ethereal solution has a certain degree of stability; so that the presence of peroxide of hydrogen, in any liquid, may be ascertained by mixing it with ether, and then adding a few drops of a solution of chromic acid, whereby the ether assumes a bright blue colour.

The compound radicle, peroxide of hydrogen HO, is equivalent to the simple radicle, chlorine Cl, and in a great number of reactions is exchangeable for chlorine and its congeners. One of the most generally useful modes of oxygenating different compounds consists in first substituting a halogen in exchange for hydrogen, and then, by means of water, substituting peroxide of hydrogen in exchange for the halogen. Thus, by the action of bromine upon acetic acid, we obtain bromacetic acid:—

$$C_2H_4O_2 + Br_2 = C_2H_3BrO_2 + HBr.$$

Then by the action of water upon bromacetic acid we obtain glycolic, or oxyacetic acid:—

$$C_2H_3BrO_2 + H.HO = C_2H_3(HO)O_2, \text{ or } C_2H_4O_3 + HBr.$$

It is observable that water may be regarded as a derivative of chlorhydric acid, in which the compound radicle HO, replaces the simple radicle Cl, and so in other instances, thus:—

Chlorhydric acid	H.Cl	H.HO	Water.
Chlorine	Cl.Cl	HO.HO	Peroxide of hydrogen.
Chloride of ethyl	C_2H_5.Cl	C_2H_5.HO	Alcohol.
Chloride of benzoyl	C_7H_5O.Cl	C_7H_5O.HO	Benzoic acid.
Chloride of sulphuryl	SO_2''.Cl_2	SO_2''.$(HO)_2$	Sulphuric acid.
Chloride of phosphoryl	PO'''.Cl_3	PO'''.$(HO)_3$	Phosphoric acid.

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Oxides and Hydrates.

(130) Starting from chlorhydric acid HCl, we have seen that the principal varieties of chlorides are the protochlorides, the bichlorides, and the terchlorides, with which last may be associated the sesquichlorides. Similarly, starting from water H_2O, as a type, we have three principal varieties of oxides, thus:—

HCl Chlorhydric acid.	H_2O Water.
$ZnCl$ Protochloride of zinc.	Zn_2O Protoxide of zinc.
$PtCl_2$ Bichloride of platinum.	Pt_2O_2 Binoxide of platinum.
$BiCl_3$ Terchloride of bismuth.	Bi_2O_3 Teroxide of bismuth.
Fe_2Cl_3 Sesquichloride of iron.	Fe_4O_3 Sesquioxide of iron.

It is observable that while in the chlorides the replaceable hydrogen is indivisible, in the oxides it may be, and frequently is, represented by two or more different elements. Thus, taking the simplest type, namely the single atom of water, we can have the following derivatives:—

Type.	H_2O Water.
Basic hydrates and oxides, or bases	KHO Hydrate of potassium.
	K_2O Oxide of potassium.
Acid hydrates and oxides, or oxacids and anhydrides .	$HClO$ Hypochlorous acid.
	Cl_2O Hypochlorous anhydride.
Saline oxides, or oxysalts .	$KClO$ Hypochlorite of potassium.

Thus, even from the simplest type H_2O, we can derive several different kinds of oxides, while from the more complex multiple types H_4O_2, H_6O_3, we may obtain varieties that are almost innumerable. We must postpone our consideration of the general properties of oxacids and oxysalts, and content ourselves, for the present, with reviewing the principal classes of more or less basic oxides, their properties and modes of formation. It is observable that the distinctions between basic, acid, and saline oxides are chiefly of a conventional character. Analogically all these bodies belong to the one single class, that of oxides. But we find that some hydrates have a marked tendency to exchange their hydrogen for a metallic, or basylous, or electro-positive element. These constitute the acid hydrates, or more simply the acids. Basic hydrates, on the other hand, have a marked tendency to exchange their hydrogen for a chlorous, or acid, or electro-negative element, or radicle. But basylous and chlorous elements, as has been already observed, and consequently acid and basic hydrates, shade off into one another by insensible gradations, so as to prevent the possibility of drawing any strict line of demarcation between them. In a similar manner, we are unable to define the difference between

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an oxysalt, such as chlorite of potassium $KClO_2$, and a neutral double oxide, such as chrome iron $FeCr_2O_2$, or $FeCcrO_2$. With these explanations, or reservations, we classify the more or less basylous or salifiable oxides as follows:—

a. Oxides with one atom of oxygen formed on the type of the single atom of water H_2O. All those metals which are prot-equivalent, or capable of replacing hydrogen by an exchange of atom for atom, of which the principal are lithium, sodium, potassium, calcium, strontium, barium, magnesium, zinc, cadmium, chrome, manganese, iron, nickel, cobalt, copper, mercury, lead, silver, palladium, platinum, and gold, form prothydrates, having the general formula MHO, where M stands for an atom of metal. The hydrates of lithium, sodium, potassium, calcium, strontium, and barium, are soluble in water, forming solutions which turn red litmus paper blue, turn yellow turmeric paper brown, and cause precipitates in the solutions of the salts of all other metals. The other hydrates are insoluble, or very nearly so; those of magnesium, mercury, lead, and silver, having indeed a very sparing degree of solubility. The hydrates of lithium, sodium, and potassium volatilise slightly, but do not decompose even at the highest temperatures. All other prothydrates are decomposed by heat into metallic oxide and water, the degree of heat necessary to effect the change varying in each particular instance. Thus, hydrate of copper is decomposed at a temperature below that of boiling water, 2CuHO becoming $Cu_2O + H_2O$. On the other hand, hydrate of lime requires a full red heat to yield caustic lime and water. All the metals that form prothydrates form protoxides also, having the general formula M_2O. The protoxides of lithium, sodium, potassium, calcium, strontium, and barium, are decomposed by water, with the production of soluble prothydrates. Thus, an atom of oxide of calcium or burnt lime Ca_2O, is converted by the agency of water H_2O, into two atoms of hydrate of calcium, or slaked lime 2CaHO. All other protoxides are insoluble in water, and for the most part undecomposible thereby. Oxide of magnesium, however, by the prolonged action of water, is slowly converted into hydrate of magnesium. Besides prothydrates and protoxides we have also double oxides, in which each atom of hydrogen is replaced by a different prot-equivalent metal. These compounds are of an ill-defined character: potassium-oxide of zinc KZnO, may be taken as an example. We have seen (vide par. 42, *ε*) that a few metals, notably copper and mercury, are di-equivalent, or have the property of replacing hydrogen by an exchange

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of two atoms of metal for one atom of hydrogen. Thus, besides the prothydrate Cu'HO, and the protoxide of copper $Cu_2'O$, we have a dihydrate of copper $,,Cu_2HO$, and a dinoxide of copper $,,Cu_4O$, also formed on the type of one atom of water H_2O. In the former compound one of the hydrogen atoms, and in the latter both of the hydrogen atoms are replaced respectively by two atoms of copper, having each a di-equivalent function, or being equivalent to only half an atom of hydrogen. The dinoxides and dihydrates, particularly under certain conditions, have a tendency to become decomposed into the corresponding proto-compound and metal, thus: $,,Hg_4O = Hg_2'O + Hg_2$. The protoxides, prothydrates, dinoxides, and dihydrates are decomposed by nearly all acids, with the formation of salts, and the elimination of one atom of water for each atom of oxide or hydrate, thus:—

$$\begin{aligned} CaHO &+ HCl = H_2O + CaCl \\ Ca_2O &+ 2HCl = H_2O + 2CaCl \\ ,,Hg_2HO &+ HCl = H_2O + ,,Hg_2Cl \end{aligned}$$

β. Oxides with two atoms of oxygen, formed on the type of the double atom of water H_4O_2. *a.* We have already explained (vide par. 42, *β*) that some metals, notably tin, palladium, and platinum, have, under some circumstances, the property of replacing hydrogen by a substitution of one atom of metal for two atoms of hydrogen, or, in other words, are bi-equivalent. These metals yield salifiable bihydrates and binoxides; thus we have stannous hydrate $Sn''H_2O_2$, palladic hydrate $Pd''H_2O_2$, and platinic hydrate $Pt''H_2O_2$, formed from the double atom of water H_4O_2, by the displacement of two atoms of hydrogen by one atom of a bi-equivalent metal. We have also stannous oxide $Sn^2''O_2$, palladic oxide $Pd_2''O_2$, and platinic oxide $Pt_2''O_2$, formed from the double atom of water H_4O_2, by the displacement of the four atoms of hydrogen by two atoms of bi-equivalent metal. These bihydrates and binoxides are all insoluble in water. The hydrates are decomposed by heat into water and binoxide, thus: $2Pt''H_2O_2 = 2H_2O + Pt_2''O_2$. With the above-described bihydrates and binoxides may be associated certain ill-defined double oxides, in which one pair of the hydrogen atoms of the type is replaced by one atom of a bi-equivalent metal, and the other pair of hydrogen atoms by two atoms of a prot-equivalent metal, which is usually of a markedly basylous character. Thus we have platinite of potassium $K_2Pt''O_2$, stannite of sodium $Na_2Sn''O_2$, &c. This H_4O_2 type also embraces the large class of oxides known as $\frac{3}{4}$-oxides, compounds in

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which three atoms of hydrogen are replaced by one atom of a ter-equivalent metal, or by the double atom of a sesqui-equivalent metal, while the fourth atom of hydrogen in the type either remains, or is replaced by one atom of a prot-equivalent metal.* Examples of these compounds are furnished us by magnetic oxide of iron $Fe(Fe_2)'''O_2$, chrome iron $Fe(Cr_2)'''O_2$, brown hæmatite $H(Fe_2)'''O_2$, bismuthite of sodium $NaBi'''O_2$, &c. Some of the native $\frac{3}{4}$-oxides are very slowly attacked by acids; but all the oxides of this class as yet referred to, binoxides, bihydrates, and $\frac{3}{4}$-oxides, when decomposed by acids, form salts corresponding to the acids, and eliminate two atoms of water for each atom of oxide decomposed, thus: —

$$Pt_2''O_2 + 4HCl = 2H_2O + 2Pt''Cl_2$$
$$Fe'(Fe_2)'''O_2 + 4HCl = 2H_2O + FeCl + (Fe_2)'''Cl_3.$$

b. In addition to these salifiable binoxides, there are certain other oxides with two atoms of oxygen, possessed of very different properties. In these last binoxides, typified by peroxide of hydrogen H_2O_2, the second atom of oxygen seems to be retained on a very uncertain tenure. Binoxides of this description are usually termed peroxides, to distinguish them from the salifiable binoxides already considered. These peroxides do not form any corresponding chlorides, or corresponding salts in general. Hence, when acted upon by chlorhydric acid, for instance, they form not bichlorides but protochlorides, and evolve either peroxide of hydrogen or chlorine, thus: —

$$Ba_2O_2 + 2HCl = H_2O_2 + 2BaCl$$
$$Mn_2O_2 + 4HCl = 2H_2O + 2MnCl + Cl_2.$$

The peroxides of barium, strontium, calcium, potassium, and sodium have a tendency to produce peroxide of hydrogen; while the peroxides of the less basylous metals, manganese, lead and silver, have a tendency to produce chlorine. But this difference is not one of a markedly distinctive character, for all peroxides alike evolve chlorine, when heated with strong chlorhydric acid. All

* The name $\frac{3}{4}$-oxides was originally applied to these compounds from a numerical relation existing between the oxygen and metal in their formulæ, which the system of notation employed in this work has caused to disappear. The name may, however, be retained in a different sense, as implying that, in these oxides, a single ter-equivalent, or sesqui-equivalent metal replaces three-fourths of the hydrogen of the type, H_4O_2.

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peroxides, also, whether of the more or less basylous sub-groups, alike yield oxygen and a protosulphate when acted upon by strong sulphuric acid: —

$$Ba_2O_2 + H_2SO_4 = H_2O + O + Ba_2SO_4.$$
$$Mn_2O_2 + H_2SO_4 = H_2O + O + Mn_2SO_4.$$

The oxygen evolved from the above reaction with peroxide of barium is highly ozonic, and that from the reaction with peroxide of manganese appears to contain a trace of ozone.

We might classify these peroxides as a distinct group, and assign to them a distinct set of formulæ, thus: —

$H_2\ O.O$	Peroxide of hydrogen.
$Na_2O.O$	Peroxide of sodium.
$K_2\ O.O$	Peroxide of potassium.
$Ca_2\ O.O$	Peroxide of calcium.
$Sr_2\ O.O$	Peroxide of strontium.
$Ba_2\ O.O$	Peroxide of barium.
$Mn_2O.O$	Peroxide of manganese.
$Pb_2\ O.O$	Peroxide of lead.
$Ag_2O.O$	Peroxide of silver.

We find, however, that although non-salifiable as a rule, yet under certain circumstances, some of these oxides can act as if salifiable. Thus the peroxides of manganese and lead are capable of dissolving in acetic acid to form binacetates. Moreover, the acknowledged salifiable binoxide of palladium manifests many of the properties of a peroxide. Whence it seems that the difference between a salifiable binoxide and a neutral peroxide is rather a difference of habit than of essential character; and this view is confirmed by a consideration of the peroxides with three atoms of oxygen belonging to the next group. Most of the above peroxides can exist in the hydrated state, but whether or not the water exists as a separate constituent has not been satisfactorily ascertained. Some oxides also, having the formulæ of $\frac{3}{4}$-oxides, have the characters of peroxides. Thus, red oxide of lead has a formula corresponding to that of black oxide of iron, but the two bodies behave very differently when treated with acids. The former breaks up in accordance with this equation: —

$$2Pb_3O_2 = \underset{\text{Non-salifiable.}}{2Pb_2O} + Pb_2O_2;$$

the latter in accordance with this: —

$$2Fe_3O_2 = \underset{\text{Salifiable.}}{Fe_2O} + Fe_4O_3.$$

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c. There are several metallic, or pseudo-metallic, oxides with two atoms of oxygen and one atom of metal, which have an acid rather than a basic character, and correspond with chlorides having four atoms of chlorine. They are principally the following: —

SeO_2	Selenious anhydride.
TeO_2	Tellurous anhydride.
SiO_2	Silica.
SnO_2	Stannic anhydride.*
TiO_2	Titanic anhydride.
ZrO_2	Zirconia.
TaO_2	Tantalic anhydride.

γ. Oxides with three atoms of oxygen formed on the type of three atoms of water, H_6O_3. *a.* In this class are included salifiable teroxides and terhydrates, sesquioxides and sesquihydrates. The teroxide of bismuth $Bi_2'''O_3$ is the most basylous of the teroxides. In the teroxides of gold and antimony, $Au_2'''O_3$ and $Sb_2'''O_3$ respectively, the chlorous and basylous functions are pretty equally balanced, while in teroxide of arsenic $As_2'''O_3$ the basylous character is scarcely to be recognised. This last teroxide is sparingly soluble in water, being converted by solution into its corresponding hydrate or acid, thus: $As_2'''O_3 + 3H_2O = 2H_3As'''O_3$. The more basylous teroxides are practically insoluble in water, that of bismuth entirely so. They all form hydrates, of which, however, the composition has not been positively ascertained. That of bismuth, when first precipitated, is probably $H_3Bi'''O_3$, but by drying it loses water H_2O, and becomes the $\frac{1}{4}$-compound $HBi'''O_2$. The principal salifiable sesquioxides are those of aluminum, iron, chromium, and cerium, which may be thus formulated: —

Al_4O_3	or	$(Al_2)_2O_3$	or	$All_2'''O_3$.
Fe_4O_3	„	$(Fe_2)_2O_3$	„	$Ffe_2'''O_3$.
Cr_4O_3	„	$(Cr_2)_2O_3$	„	$Ccr_2'''O_3$.
Ce_4O_3	„	$(Ce_2)_2O_3$	„	$Cee_2'''O_3$.

The corresponding sesquihydrates are $H_3All'''O_3$, $H_3Ffe'''O_3$, $H_3Ccr'''O_3$, and $H_3Cee'''O_3$ respectively. These normal hydrates are somewhat unstable, especially on the application of heat,

* It is doubtful whether the molecule of stannous oxide ought not to be represented by the formula SnO, rather than by Sn_2O_2. In this case the principal varieties of salifiable oxides might be typified as follows:—

Sn O	Sn O_2	Te O_3
Fe_2O	Pt_2O_2	Sb_2O_3
Cu_4O	Fe_3O_2	Fe_4O_3

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whereby they lose water and become $\frac{3}{4}$-compounds. For example, $H_3Ffe'''O_3$, when dried at 120° loses H_2O, and becomes $HFfe'''O_2$. By a further application of heat they are rendered anhydrous, thus:—

$$2H_3Ffe'''O_3 - 3H_2O = Ffe_2'''O_3, \text{ or } Fe_4O_3.$$

The sesquihydrates are all readily soluble in acids. The sesquioxides exist in several different modifications, some of which are readily, others scarcely at all, acted upon by acids. But all salifiable oxides and hydrates with three atoms of oxygen, when decomposed by acids, yield corresponding salts, and eliminate three atoms of water, thus:—

$$Bi_2'''O_3 + 6HCl = 3H_2O + 2Bi'''Cl_3$$
$$H_3All'''O_3 + 3HCl = 3H_2O + All'''Cl_3, \text{ or } Al_2Cl_3.$$

b. Certain sesquioxides have the characters of peroxides; that is to say, when acted upon by acids, they do not form sesquisalts but protosalts, and simultaneously evolve oxygen or chlorine. The sesquioxides of cobalt and nickel Co_4O_3 and Ni_4O_3 respectively, are as decidedly peroxides as are the binoxides of lead and barium. The sesquioxide of manganese is intermediate in its properties, and serves to connect the salifiable sesquioxides of chrome and iron with the indifferent sesquioxides, or peroxides, of nickel and cobalt. Thus it dissolves in cold chlorhydric acid to form an unstable hydrated sesquichloride of manganese:—

$$Mn_4O_3 + 6HCl = 3H_2O + 2Mn_2Cl_3.$$

But when heated with chlorhydric acid, it forms protochloride of manganese and chlorine:—

$$Mn_4O_3 + 6HCl = 3H_2O + 4MnCl + Cl_2.$$

c. Certain oxides with three atoms of oxygen react in a very peculiar manner with acids, as if two-thirds of the oxygen were retained by the metal on a more intimate footing than the remainder. Sesquioxide of uranium U_4O_3, is the most striking member of this class. To judge from its reactions, it would seem to be the protoxide of an oxidised radicle U_2O, playing the part of a metal. This sesquioxide might be represented by the formula $(U_2O)_2O$, analogous to that of protoxide of copper $(Cu)_2O$, in which the compound radicle U_2O plays the part of metallic copper Cu. Certain it is that the grouping U_2O is capable of being

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transferred from one compound to another in exchange for an atom of hydrogen or its representative, precisely as is the metal copper, thus:—

$$(Cu)_2O + 2HNO_3 = H_2O + 2(Cu)NO_3$$
$$(U_2O)_2O + 2HNO_3 = H_2O + 2(U_2O)NO_3.$$

In a similar manner, the teroxide of antimony occasionally, and the sesquioxide of iron more rarely, react as if their respective formulæ were $(SbO)_2O$ and $(Fe_2O)_2O$. In many aluminous silicates also, the sesquioxide of aluminum Al_4O_3, appears to function as a protoxide of aluminyl $(Al_2O)_2O$. The peculiarity of the sesquioxide of uranium is that it never acts as a salifiable sesquioxide, but always as an oxide of uranyl. Oxides behaving in the above-described manner were termed by Laurent basyl-oxides, and their corresponding salts basyl-salts.

The same metal may give origin to many different oxides and hydrates, as instanced particularly by the metal manganese. The protoxides and prothydrates are the most strongly basylous, and then follows the sesquioxides. The acid characters of the hydrates increase with the relative proportion of oxygen which they contain:—

H Mn O	Manganous hydrate	Mn_2O	Protoxide
H Mn_2O_2	Manganic hydrate	Mn_3O_2	¾-oxide
$H_2Mn_2O_4$	Manganic acid	Mn_4O_3	Sesquioxide
H Mn_2O_4	Permanganic acid	Mn_2O_2	Peroxide

Other oxides and hydrates of manganese also exist, which are less familiarly known to chemists.

The relations to one another of the principal classes of chlorides and salifiable oxides and hydrates are shown in the following table:—

	Chloride.	Hydrate.	Oxide.
Proto	Zn′ Cl	H Zn′ O	Zn_2' O
Di	„Cu_2 Cl	H„Cu_2 O	„Cu_4 O
Bi	Pt″ Cl_2	H_2Pt'' O_2	Pt_2'' O_2
¾	—	H Bi‴ O_2	Fe Ccr‴ O_2
Ter	Sb‴ Cl_3	H_3Sb''' O_3	Sb_2''' O_3
Sesqui	Ffe‴Cl_3	$H_3Ffe'''O_3$	Ffe_2''' O_3
	Fe_2 Cl_3	H_3Fe_2 O_3	Fe_4 O_3

(131) Some metallic oxides are found native. The principal of these are certain oxides of iron, namely, the sesquioxide Fe_4O, known as red hæmatite or oligiste, the hydrated sesquioxide $H(Fe_2)'''O_2$, known as brown hæmatite or brownstone, the ¾-oxide $Fe(Fe_2)'''O_2$, known as magnetic iron ore,—and certain oxides of manganese, namely, the peroxide Mn_2O_2, known as pyrolusite,

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and several rarer oxides, including the sesquioxide or braunite Mn_4O_3, the hydrated sesquioxide or manganite $H(Mn_2)'''O_2$, the $\frac{3}{4}$-oxide or hausmannite $Mn(Mn_2)'''O_2$, and an oxide of peculiar composition, known as varvicite. The principal source of tin is the native binoxide SnO_2, or tinstone; of chromium, the native double oxide of chrome and iron $Fe(Cr_2)'''O_2$, or chrome-iron; and of uranium, the native $\frac{3}{4}$-oxide $U(U_2)'''O_2$, or pitchblende. Sesquioxide of aluminum Al_4O_3, occurs native in the forms of ruby, sapphire, and corundum; and combined with oxide of magnesium in spinelle $Mg(Al_2)'''O_2$. Moreover, native alumina and native magnesia occur in the hydrated state, the former as diaspore, the latter as brucite. Native teroxides of antimony and bismuth have been occasionally met with, as have also the two oxides of copper. Binoxide of titanium is found native as rutile, brookite, and anatase.

(132) Metallic oxides are obtained artificially by the following processes. *a.* The soluble hydrates of calcium, strontium, and barium are usually prepared by the action of water upon the anhydrous protoxides. The soluble hydrates of lithium, sodium, and potassium might be made in a similar way, but in practice are always obtained by decomposing solutions of their carbonates, sulphates, or sulphydrates by other bases. Thus the carbonate of alkali-metal is usually decomposed by lime or barytes, the sulphate by barytes, and the sulphydrate by oxide of copper. Hydrate of barium likewise is frequently made by decomposing the sulphide or sulphydrate of barium with oxide of copper. The six soluble hydrates also result from the action of water at ordinary temperatures upon their respective metals. The insoluble salifiable hydrates are prepared by decomposing some or other of their salts, with the above soluble hydrates, or with ammonia, or in some cases with magnesia. Moreover, the carbonates of the corresponding basylous metals may be substituted for the above hydrates to precipitate those hydrated oxides which do not readily combine with carbonic anhydride to form carbonates, thus:—

$$SnCl_2 + H_2O + Ca_2CO_3 = 2CaCl + H_2Sn''O_2 + CO_2$$
$$2Fe_2Cl_3 + 3H_2O + 3Ca_2CO_3 = 6CaCl + 2H_3(Fe_2)'''O_3 + 3CO_2.$$

And, in a few cases, water, especially boiling water, may be substituted for the alkali, thus:—

$$Bi'''(NO_3)_3 + 3H_2O = 3HNO_3 + H_3Bi'''O_3.$$

Nitrate of tellurium is decomposed by water in a somewhat similar manner.

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The hydrated peroxides are usually prepared by adding water to the anhydrous peroxides of the highly basylous metals; or by precipitating their soluble salts with peroxide of hydrogen; or by passing chlorine gas through the protoxides of the heavy metals suspended in water or alkaline liquid:—

$$Cl_2 + 2KHO + 2Co_2O = 2KCl + Co_4O_3.H_2O.$$

The prothydrates of iron and manganese absorb oxygen from the air to form their respective sesquihydrates.

β. Anhydrous oxides are frequently prepared by directly oxidising the metal. Many oxides, especially those of volatile metals, arsenic, zinc, cadmium, and mercury for instance, are obtained by simply heating the metals in air or oxygen. Protoxide of lead, a readily fusible oxide, is made commercially by roasting the metal in a current of air. Black oxide of iron is well known in the form of smithy scales, as a product of the ignition of iron in the atmosphere; and the two oxides of copper may be made in a similar manner. Sometimes, also, the metallic oxides result from the direct action of oxygen upon certain compounds of the metals. Thus arsenious anhydride, and the mixed oxides of iron and copper, are prepared by roasting metallic sulphides instead of the reguline metals. Again, peroxide of silver is made by acting upon nitrate of silver with nascent oxygen, evolved from the positive plate of the battery. Many oxides, procured in various ways, are converted into their higher oxides by ignition in a current of oxygen or of air, as is the case with oxide of barium and oxide of lead, for instance. In these direct modes of oxidation, the oxygen is frequently supplied by means of some oxidising compound. Thus the oxides of tin and antimony are readily made by acting upon the respective metals, or their sulphides, with strong nitric acid; and many oxides are procured by fusing the metals, or their sulphides, with nitre. By this last method, the resulting oxides, if at all of an acid-forming character, appear in the state of potash salts. We have already observed that many metals, especially at a red heat, are readily oxidated by water or steam.

γ. Some oxides are made, not by oxidation, but by reduction of their superior oxides. Thus the $\frac{3}{4}$-oxide of manganese is made by igniting the peroxide. Sesquioxide of chrome is made by igniting chromic acid, or the chromates of the volatile metals, mercury and ammonium. Dinoxide of copper is made by reducing the protoxide with metallic copper. Binoxide of tungsten is made by reducing tungstic anhydride in a current of hydrogen. Sometimes the hydrogen resulting from the decomposition of ammonia effects the

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reduction. In this way the ignition of the molybdate of ammonia yields the protoxide of molybdenum.

δ. One of the most common methods of preparing anhydrous metallic oxides consists in heating metallic hydrates, carbonates, oxalates, nitrates, and sulphates. Nearly all metallic hydrates yield metallic oxide by exposure to a degree of heat varying from below 100° to full redness. The hydrates of potassium, sodium, and lithium are not decomposed by heat, but can yield their corresponding oxides by treatment with their respective metals: $NaHO + Na = Na_2O + H$. With the exception of barium, potassium, sodium, and, to some extent, lithium, all metallic carbonates are decomposed by heat and yield metallic oxide. Quicklime or protoxide of calcium is made in this way by the ignition of chalk or carbonate of calcium. The oxides of nickel and cobalt are frequently prepared by igniting their oxalates; those of barium, copper, and mercury, by igniting their nitrates; and those of iron and aluminum by igniting their sulphates.

(133) Oxides are for the most part opaque earthy bodies, destitute of metallic lustre. With the exception of the peroxides of silver, lead, and manganese, they are non-conductors of electricity. The densities of metallic oxides, save of the highly basylous ones, are usually lower than those of the metals themselves. Some native oxides are extremely hard. This hardness greatly exceeds, but otherwise bears no relation to, the hardness of the corresponding metals. At ordinary temperatures, all metallic oxides occur in the solid state. The majority of them are fusible, those of lead and bismuth at a low red heat, those of copper and iron at a white heat, those of barium and aluminum in the oxyhydrogen blowpipe, but that of calcium at no temperature to which it has hitherto been subjected. Unlike the combinations of metal with chlorine, which are much more fusible, the combinations of metals with oxygen, except indeed the black oxide of iron, the sesquioxide of chrome, and the teroxide of molybdenum, are much less fusible than the uncombined metals. The tessaroxides of osmium and ruthenium, the teroxides of arsenic and antimony, and the binoxide of tellurium are readily volatile.

A greater or less degree of temperature effects the decomposition of many metallic oxides. Those of gold, platinum, silver, and mercury are reduced to the reguline state by an incipient red heat. At a somewhat higher temperature, the peroxides of barium, cobalt, nickel, and lead are reduced to the state of protoxides; while the $\frac{3}{4}$-oxides of manganese and iron result from the exposure of the binoxide and sesquioxide respectively to a still stronger degree of heat.

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By gentle ignition, arsenic anhydride is reduced to the state of arsenious anhydride, and chromic anhydride to the state of sesquioxide of chromium.

The superior oxides of the metals are readily reduced to a lower state of oxidation by treatment with a current of hydrogen gas at a more or less elevated temperature. At a high degree of heat, hydrogen gas will transform to the reguline state all metallic oxides except the sesquioxides of aluminum and chrome, and the protoxides of manganese, magnesium, barium, strontium, calcium, lithium, sodium, and potassium. But the temperature necessary to enable hydrogen to effect the decomposition of some oxides is comparatively low. Thus even metallic iron may be reduced from its oxides by hydrogen gas at a heat considerably under redness, so as to form an iron pyrophorus. Carbon, at a red or white heat, is a still more powerful deoxidating agent than hydrogen, and seems to be capable of completely reducing all metallic oxides whatsoever. In the reduction of metallic oxides by carbon at a high temperature, carbonic oxide is always produced, the reducing power of which gas also is extremely great. The oxidisable metals in general act as reducing agents. As a rule, the more basylous metals, when heated with the oxides of less basylous metals, reduce the latter to the reguline state. Many inferior oxides, dinoxide of copper for instance, are made by reducing the higher oxides with metal.

With the exception of the oxides of the earth-metals, chlorine decomposes all metallic oxides, uniting with the metals to form chlorides, and expelling the oxygen. With oxide of silver this reaction takes place at ordinary temperatures; with the alkalies and alkaline earths, at a full red heat. The action of chlorine upon metallic hydrates and moist metallic oxides, to form metallic chlorides and either hypochlorites or peroxides, has been already described. Sulphur at an elevated temperature can decompose most metallic oxides. With many oxides, those of silver, mercury, lead and copper, for instance, sulphide of metal and sulphurous anhydride are produced. With the highly basylous oxides, the products are metallic sulphate and sulphide. There are some oxides upon which sulphur exerts no action. Of these the principal are magnesia, alumina, chrome, and the stannic and titanic anhydrides. By boiling sulphur with soluble hydrates, mixtures of polysulphide and thiosulphate are produced. With the exception of magnesia, alumina, and chrome, most metallic oxides can absorb sulphuretted hydrogen, to form metallic sulphide or sulphy-

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drate and water. The action of phosphorus upon metallic oxides, at a red heat, is very analogous to that of sulphur. It usually produces a mixture of phosphide and phosphate. Like sulphur, it does not react with magnesia and alumina. Boiled with the soluble alkalies, it produces phosphuretted hydrogen and a hypophosphite. The action of water and acids upon metallic oxides has been considered in the section devoted to their classification (vide par. 130). Many of the acid-forming metallic oxides or anhydrides dissolve in water to a greater or less extent, undergoing decomposition, and producing acid solutions. But the binoxides of tin, titanium, zirconium, and tantalum, and the teroxides of tellurium and tungsten may be obtained in a state perfectly insoluble in water.

§ II. Sulphur.

Symbol, S; *Proportional number*, 32; *Vapour-density*, 32; *Atomic volume*, □.

(134) Sulphur (*sal*, *πῦρ*), or brimstone (*brennestone*), has been known from the earliest times. It occurs native, either in the form of transparent amber-coloured crystals (*virgin sulphur*), or in opaque, lemon-yellow, crystalline masses (*volcanic sulphur*). It is found principally in Sicily, in beds of a blue clay formation, considered to be more recent than the chalk. The sulphur is imbedded in a matrix of rock-salt, gypsum, and celestine. Similar beds containing sulphur exist in other parts of Europe. It is also found occasionally in primitive rocks, granite, mica, &c. It abounds in the lava-fissures of volcanic craters, as instanced especially in the case of the Solfatara near Naples (*Forum Vulcani*). Sulphur also occurs native in combination with different metals, forming metallic sulphides, of which the principal are blende, iron-pyrites, copper-pyrites, galena, cinnabar, grey antimony, and realgar. Sulphydric acid occurs in hepatic mineral waters, and among the products of animal decomposition. Sulphurous acid is a frequent constituent of volcanic emanations, and free sulphuric acid is sometimes found in the waters of volcanic neighbourhoods. Gypsum, celestine, and heavy spar constitute well-known minerals; and, in addition to gypsum, the sulphates of magnesium and sodium are very common ingredients of mineral waters. Sulphur

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exists in the protein compounds of animal and vegetable organisms, in the taurine of bile, in the cystine of urine, and in the alliaceous volatile oils.

(135) Native sulphur is sometimes purified by a rough process of fusion, effected on the spot where it is obtained. A heap is set fire to, whereby the heat evolved from the burning of one portion fuses the remainder. It is more usual, however, to purify it by distillation in upright earthen pots, or retorts, set back to back, in two rows, in a long brick furnace. The distillate is received in somewhat similar pots, arranged in two rows outside the furnace, and furnished each with an opening near its base through which the sulphur, condensed within the pot, flows into a pail of water in which it congeals. The sulphur thus purified by fusion or distillation is known as rough sulphur, and contains about 3 per cent. of foreign matter. It is further purified by redistillation in an iron still. The vapours are sometimes received in a large brick chamber, within which the sulphur condenses in a pulverulent state to constitute flowers of sulphur, or sublimed sulphur; or it is condensed in the liquid state in a smaller and hotter receiver, and is either cast into sticks, when it constitutes roll sulphur, or is allowed to congeal in mass, when it constitutes refined lump sulphur.

(136) *a.* Sulphur may be obtained by heating bisulphide of iron in close vessels, precisely as oxygen is obtained by heating binoxide of manganese under similar conditions:—

$$3Fe_2S_2 = 2Fe_3S_2 + S_2.$$

Manufactured sulphur is made principally from copper pyrites, a double sulphide of copper and iron, as a preliminary stage in the process of copper smelting. Upon a layer of broken pyrites is placed a layer of brushwood, and on this is constructed a huge pyramidal pile of ore, having a central wooden chimney communicating with air passages left among the brushwood. The whole pile is covered with powdered ore, and the mass set fire to by dropping down lighted faggots through the chimney. As the slow combustion of the pile proceeds, sulphur gradually trickles down and is collected in cavities made extempore in the walls of the heap, whence it is ladled out into moulds. Such a heap, consisting of some 2000 tons of ore, will continue burning for five or six months, and will yield about 20 tons of rough sulphur, which may be purified by fusion or distillation. Copper pyrites is sometimes roasted for the extraction of sulphur in a tall domed furnace, from the summit of which a horizontal flue conveys the sulphur vapours into a chamber, within

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which they are condensed. The sulphur obtained from pyrites is partly expelled by heat, partly displaced by oxygen.

β. Sulphur is also prepared in this country from the decomposition, by exposure to air, of the hydrated sulphide of iron, resulting from the purification of crude coal gas with ferric oxide or hydrate:—

$$2Fe_2S + H_2O + O_3 = 2HFe_2O_2 + S_2.$$

The hydrate of iron produced in the above reaction is again used to purify the crude gas, whereby it becomes converted into sulphide, and this sulphide is then reconverted into oxide and sulphur by exposure to air as before. These alternate processes are repeated an indefinite number of times, until the amount of sulphur in the material reaches from 40 to 50 per cent, when it is distilled off in iron retorts.

γ. Sulphur results from a great number of other reactions, which, however, are not usually employed for its commercial preparation. Thus it may be obtained by decomposing an alkaline polysulphide with an acid; by the mutual reaction of sulphurous and sulphydric acids; by treating sulphydric acid with almost any oxidising agent; by the decomposition of the chlorides of sulphur with water; by the spontaneous decomposition of thiosulphuric, or hyposulphurous, acid; by the ignition of the tri-, tetra-, and, pentathionates, &c. &c.

(137) At ordinary temperatures, sulphur is a very brittle solid, of a lemon-yellow colour, tasteless from its insolubility in water, and almost inodorous. It is a bad conductor of heat, and a non-conductor of electricity. By friction with wool or hair it becomes negatively electric. Its sp. gr. in the native crystalline state is 2·05. It begins to melt at 114·5°, and at 120° is converted into a perfectly limpid, pale yellow liquid, which is lighter than solid sulphur. Provided the temperature of 120° has not been much exceeded, it resolidifies suddenly at that same temperature into a transparent mass, which retains its transparency for a long time. By heating sulphur to a temperature much above 120°, its congealing point is lowered to 111·5°, from the production of a peculiar modification of the element. Sulphur which has been congealed at this low temperature is at first transparent, but becomes opaque much more rapidly than does that which has been congealed at 120°. As melted sulphur is gradually heated above 120°, it gradually becomes darker and more viscid, until at the temperature 200—250°, it is so thick that the flask in which it is contained may be inverted

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without any outflow taking place. The temperature of maximum viscidity remains constant for some time, owing to a considerable absorption of latent heat. At from 250° to 300° and upwards, the sulphur again liquefies, but does not become so fluid as at 115—120° when first melted. On cooling it passes inversely through the same changes of state. Sulphur boils at 440°, and is converted entirely into an orange-coloured vapour. According to Bineau, whose statement has been recently confirmed by Deville and Troost, the density of sulphur-vapour, when taken at the temperature of 1000°, is 32 times as great as that of hydrogen at the same temperature; but its density taken at about 500° is anomalous, being three times as great as it should be theoretically. Sulphur vaporises to a slight extent at ordinary temperatures; so that a piece of silver leaf, suspended at some distance above a stick of sulphur, becomes slowly transformed into sulphide of silver.

(138) Sulphur is remarkable for the great number of allotropic forms in which it can exist. Of these, however, there are two principal well-characterised varieties, namely, the soluble and insoluble, and many minor modifications. Berthelot distinguishes the soluble variety by the name of electro-negative sulphur, because it is the form which appears at the positive pole of the battery during the electrolysis of sulphydric acid, and which is separated from the combinations of sulphur with the electro-positive metals. The insoluble variety he distinguishes as electro-positive sulphur, because it is the form which appears at the negative pole during the electrolysis of sulphurous anhydride, and which separates from the combinations of sulphur with the electro-negative elements, chlorine, bromine, oxygen, &c. The following are the most important modifications of soluble sulphur. The *octahedral* variety, frequently represented by the symbol Sα, which is the most stable, and the one into which all the other varieties, soluble or insoluble, tend to change. It is the form in which native sulphur is found, and in which the crystals of sulphur obtained by the spontaneous evaporation of its solution in bisulphide of carbon are usually deposited. Its sp. gr. is 2·05, and its melting point, according to Brodie, 114·5°. It is readily soluble in bisulphide of carbon, bisulphide of chlorine, benzine, turpentine, petroleum, &c.; slightly soluble in alcohol and ether. Its crystalline form is that of an elongated octahedron on a rhombic base, belonging to the right prismatic system. The *oblique prismatic* variety, often represented by the symbol Sβ, may be obtained by the slow cooling of melted sulphur, or by heating octahedral sulphur for some time to a temperature of 105—115°. If, when a few

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pounds of melted sulphur have been allowed to cool slowly until a crust has formed on the surface, that superficial crust be broken, and the still liquid sulphur be poured out from the interior, the solidified walls will be seen to be lined with transparent yellowish-brown needles, crystallised in secondary forms of the rhombic prism, belonging to the oblique prismatic system. The sp. gr. of prismatic sulphur is 1·98. According to Brodie, when free from plastic sulphur, the presence of which lowers its melting point to 111·5°, it melts and resolidifies at 120°. It dissolves readily in bisulphide of carbon and other menstrua. In the course of a few days, this prismatic form of sulphur becomes spontaneously converted into the octahedral variety, the conversion being attended with a development of heat, which is most evident when the change is effected artificially by scratching the crystals. Opaque yellow spots first make their appearance, and then gradually spread throughout the mass. The crystals retain their prismatic shape, but on examination are found to be converted into aggregations of minute octahedrons. Conversely, a transparent crystal of octahedral sulphur, when heated to 105—115°, becomes transformed into an opaque mass of oblique prismatic crystals. When a saturated solution of sulphur in hot turpentine is allowed to cool, the crystals first deposited are of the prismatic, those last deposited, when the liquid has become comparatively cool, of the octahedral variety. Occasionally a few transparent, primary, oblique prismatic crystals are deposited from the solution of sulphur in bisulphide of carbon, but they soon break up into opaque aggregations of minute octahedrons. Roll sulphur when first cast is of the oblique prismatic, but by keeping it becomes of the octahedral variety. Its molecular condition, however, is unstable, like that of unannealed glass, whence it retains for a long time the sp. gr. of the prismatic modification. The *amorphous soluble* variety of sulphur is precipitated in the form of white emulsion, on the addition of acids to diluted solutions of alkaline polysulphides:—

$$K_2S_5 + 2HCl = 2KCl + H_2S + S_4.$$

When examined microscopically, it is found to consist of minute granules devoid of any crystalline character. It is readily soluble in bisulphide of carbon and other menstrua. This form of sulphur has a greenish white colour, and is known familiarly by the name of milk of sulphur. By keeping, it becomes gradually converted into octahedral crystals. Sublimed sulphur appears to be allied to this form. It consists of much larger granules, neither the surface nor the fracture of which is crystalline. Sublimed sulphur always contains a minute proportion of one of the insoluble modi-

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fications of the element. Vapour of sulphur, when suddenly cooled by contact with a cold surface, condenses in the form of utricles, or of liquid drops surrounded by solid pellicles. These often retain their liquidity for a considerable time, but, when solidified, seem to have the same character as the granules of sublimed sulphur. By keeping they become crystalline in the octahedral form.

The principal modifications of insoluble sulphur are the following: — The *amorphous insoluble* variety, the most stable form of which is obtained as a soft magma, by decomposing bisulphide of chlorine with water: —

$$2S_2Cl_2 + 3H_2O = 4HCl + H_2S_2O_3 + S_2.$$

The thiosulphuric, or hyposulphurous, acid, produced in the reaction, is gradually decomposed into sulphurous acid and sulphur, thus: $H_2S_2O_3 = H_2SO_3 + S$. The sulphur, resulting in this way from the spontaneous decomposition of thiosulphuric acid, has the same characters as that formed by the original decomposition of the bisulphide of chlorine. It may be obtained at once by adding dilute chlorhydric acid to the solution of a thiosulphate. If, in preparing amorphous soluble sulphur, by adding an acid to the solution of an ordinary alkaline polysulphide containing some thiosulphate, any excess of acid be added, some of this insoluble variety will also be precipitated. The above form of sulphur has a yellow colour, is insoluble in bisulphide of carbon or other menstruum, and is quite amorphous. Closely allied to it are the amorphous insoluble sulphur obtained by exhausting sublimed sulphur with bisulphide of carbon and alcohol, and that obtained by exhausting reconverted plastic sulphur with bisulphide of carbon. This last is a buff-coloured powder, slightly soluble in anhydrous alcohol. Its sp. gr. is 1·95. These varieties are convertible into octahedral sulphur by fusion, or by exposure for a greater or less length of time to the temperature of 100°. *Plastic* sulphur, frequently represented by the symbol $S\gamma$, is obtained by heating melted sulphur to the temperature 260 — 300°, and then cooling it suddenly by pouring it in a very thin stream into cold water. It is thus obtained as a soft, yellowish-brown, semi-transparent mass, capable of being drawn out into fine elastic threads possessed of considerable tenacity. This sulphur has a sp. gr. 1·95, and is insoluble in bisulphide of carbon. When sulphur, heated to 300°, is suddenly cooled by a mixture of solid carbonic anhydride and ether, it solidifies into a hard perfectly transparent mass, which becomes soft and elastic at ordinary temperatures. This appears to be the

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solid state of plastic sulphur. Another form of plastic sulphur may be obtained by acting upon metallic sulphides with boiling nitric or nitro-muriatic acid. Ordinary plastic sulphur gradually returns in the course of a few hours to its brittle state, re-acquires its yellow colour, and becomes converted almost entirely into the octahedral variety, the conversion being accompanied by an evolution of heat. If plastic sulphur be heated to 100° the change takes place suddenly, and the temperature rises to 110°. According to Brodie, sulphur begins to pass into the plastic state at a temperature very little above 120°; and the gradual loss of transparency in crystallised prismatic sulphur depends upon the hardening of plastic sulphur enclosed mechanically between the crystals. Sulphur which has been converted from the plastic into the brittle state does not dissolve entirely in bisulphide of carbon, but, as has been before observed, leaves a buff-coloured residue of insoluble sulphur, the proportion of which may, it is said, be increased by frequently causing the same sulphur to assume alternately the plastic and the brittle state. The black and red modifications of sulphur described by Magnus to result, the former, from exhausting, with bisulphide of carbon, the mass produced by the frequent alternate strong heating and sudden cooling of sulphur; and the latter, from heating the black modification to a temperature of 130–150°, are considered by Mitscherlich to depend upon the presence of greasy impurities in the sulphur. When solutions of sulphydric acid and perchloride of iron are mixed together, a blue precipitate is sometimes formed, which is said to be a peculiar allotropic form of sulphur.

(139) Sulphur may be made to combine directly with the great majority of the elements. Hydrogen gas and sulphur vapour burn in one another, though not very readily, to form sulphydric acid H_2S. When melted sulphur is treated with chlorine gas, bisulphide of chlorine Cl_2S_2, is produced, and similar reactions take place with bromine and iodine. Sulphur is highly inflammable, and when heated in air or oxygen to a temperature of 250°, takes fire and burns with a clear blue, feebly luminous flame, being converted into sulphurous anhydride SO_2. Bisulphide of carbon CS_2, results from passing sulphur vapour over red-hot charcoal. Sulphur also unites directly with phosphorus, arsenic, silicon, and boron. Nearly all the metals combine directly with sulphur, either at ordinary or increased temperatures. Zinc, iron, copper, lead, silver, tin, &c., burn in sulphur vapour with great brilliancy, the combustion, save of the zinc and iron, commencing spon-

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taneously, provided the metal is in a sufficiently divided state. Moreover, mixtures of sulphur, water, and finely-divided metal, —iron or copper, for instance,—begin to react at ordinary temperatures, evolve a considerable amount of heat, and yield hydrated protosulphide. Sulphur, when acted on by strong nitric or nitromuriatic acid, at a gentle heat, is gradually dissolved, with production of sulphuric acid H_2SO_4. Caustic alkalies also dissolve sulphur readily, with formation of sulphydrate and thiosulphate of metal, thus:—

$$4KHO + S_4 = 2KHS + H_2O + K_2S_2O_3.$$

The two atoms of sulphydrate thus produced are capable of dissolving four additional atoms of sulphur to form a pentasulphide of metal and sulphydric acid: $2KHS + S_4 = K_2S_5 + H_2S$.

(140) Sulphur in its chemical relations is the representative of oxygen, to which it is equivalent, atom to atom. The two elements, though very dissimilar in their ordinary physical characters, correspond very closely in the nature of the compounds which they form, and in the properties they exhibit when both are in the gaseous state. Although sulphur rarely, if ever, displaces oxygen by direct elementary substitution, yet the two elements are mutually interchangeable by double decomposition of their respective compounds; and, in the great majority of instances, where oxygen compounds are obtainable by the addition of oxygen, analogous sulphur compounds are obtainable by the addition of sulphur. Thus, when cyanide of potassium KCN, is treated with peroxides, we obtain oxycyanate of potassium KCNO, and when treated with sulphur, or persulphides, we obtain sulphocyanate of potassium KCNS. Again, oxygen gas and sulphur vapour alike support the combustion of hydrogen, charcoal, phosphorus, and the metals, to form precisely analogous compounds. The following are a few illustrations of the number and variety of corresponding compounds to which oxygen and sulphur respectively give origin:—

KHO,	CO_2,	C_2H_6O,	Cl_3PO,	K_3PO_4,	Sb_2OS_2,	K_2SnO_3, &c.
KHS,	CS_2,	C_2H_6S,	Cl_3PS,	K_3PO_3S,	Sb_2S_3,	K_2SnS_3, &c.

An atom of sulphur being the equivalent of an atom of oxygen, is necessarily the equivalent of two atoms of hydrogen or chlorine. Thus the chloride and sulphide of triethylphosphine, Et_3PCl_2 and Et_3PS respectively, made by acting upon triethylphosphine Et_3P, by chlorine and sulphur respectively, are the strict representatives

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of one another, and so in other instances. Certain sulphur combinations, moreover, manifest a great resemblance to those of an element we have not as yet considered, namely carbon.

Sulphydric Acid.

Symbol, H_2S; *Proportional number*, 34; *Density*, 17; *Atomic volume*, □□.

(141) *a*. This compound, familiarly known as sulphuretted hydrogen, may be formed in small quantity by burning sulphur vapour in hydrogen gas, or hydrogen gas in sulphur vapour, precisely as its analogue, water, is produced under similar circumstances from oxygen and hydrogen.

β. The gas is ordinarily prepared by the action of an acid—sulphuric or chlorhydric, for instance—upon a metallic sulphide, usually that of iron or antimony. Dilute sulphuric acid acts readily upon sulphide of iron, producing even in the cold a rapid effervescence of sulphydric acid:—

$$Fe_2S + H_2SO_4 = H_2S + Fe_2SO_4.$$

Inasmuch as sulphide of iron is an artificial product, nearly always containing an excess of metallic iron in admixture, the sulphydric acid obtained from it is generally contaminated with free hydrogen; but the native crystalline tersulphide of antimony being a normal sulphide, when acted upon by boiling chlorhydric acid, yields the gas in question in a very pure state, thus:—

$$Sb_2S_3 + 6HCl = 3H_2S + 2SbCl_3.$$

The sulphydric acid obtained from either of these sources may be passed through a small quantity of water to wash it, and over chloride of calcium to render it dry. It may be collected in the gaseous state over mercury, or it may be absorbed at once into water, in which it is very soluble.

γ. Sulphydric acid, more frequently sulphydrate of ammonia, results from the spontaneous decomposition of sulphuretted organic compounds, and also from treating nonsulphuretted organic compounds with sulphur. Reinsch recommends a laboratory process for obtaining pure sulphydric acid, by heating in a glass flask a mixture of equal parts of sulphur and suet.

δ. Sulphydric acid occurs naturally, and is not unfrequently

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evolved from fumaroles and volcanoes. It exists to a considerable extent in certain mineral waters, known as hepatic waters; those of Harrogate, for instance. It is also produced spontaneously in many waters charged with organic matter and sulphates, usually sulphate of lime or gypsum.

(142) At ordinary temperatures and pressures, sulphydric acid is gaseous. It may be obtained in the liquid state by generating it in one limb of a sealed tube, from sulphuric acid and sulphide of iron freed from metallic iron, and condensing it in the other limb, which should be immersed in a freezing mixture, that of ice and salt being sufficient for the purpose; or liquid persulphide of hydrogen may be gently heated in one limb of a bent sealed tube, when it breaks up into sulphur which remains, and sulphydric acid which may be condensed in the other limb kept cool for the purpose. By the powerful refrigeration resulting from the evaporation *in vacuo* of a mixture of solid carbonic anhydride and ether, it may be solidified. Solid sulphydric acid, or sulphur-ice, is a white transparent mass which melts at $-85{\cdot}5°$. Liquid sulphydric acid is a colourless transparent fluid remarkable for its extreme thinness or mobility. Its specific gravity is 0·9 compared with that of water as 1. Sulphydric acid gas is transparent and colourless. Its density is somewhat greater than that of atmospheric air. It is characterised by an offensive odour resembling that of rotten eggs, the smell of which indeed is due to the evolution of this gas, or of its combination with ammonia. In the concentrated state it cannot be breathed with impunity, and even when much diluted it frequently gives rise to nausea and vertigo. An atmosphere containing $\frac{1}{10}$ of a per cent. of this gas proves fatal to the lower animals. Sulphydric acid is readily inflammable. It burns with a bluish flame, forming sulphurous acid, and frequently deposits free sulphur from the imperfect access of oxygen. Most metals when heated in the gas absorb the sulphur and leave the hydrogen. Cadmium or tin is generally used for the purpose: $Cd_2 + H_2S = Cd_2S + H_2$. The bulk of the resulting hydrogen is equal to that of the original sulphydric acid; or, in other words, two volumes of sulphydric acid H_2S, when acted on by metal, leave two volumes of hydrogen; whereas two volumes of chlorhydric acid HCl, when acted on by metal, leave only one volume of hydrogen, as has been previously observed. Sulphydric acid in the gaseous state, or dissolved in water, is decomposed by chlorine, bromine, and iodine, with liberation of sulphur and formation of chlorhydric, bromhydric, and iodhydric acids respectively. In a similar manner it is decomposed, with

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liberation of sulphur, by nearly all oxidising agents; and even sulphurous acid, which usually acts as a deoxygenant by absorbing oxygen, in this case acts as an oxygenant by affording oxygen: — $2H_2S + SO_2 = 2H_2O + S_3$. In some cases, however, we have a peculiar sulphur acid, the penta-thionic, formed in addition, thus: $5H_2S + 5SO_2 = 4H_2O + H_2S_5O_6 + S_5$. A saturated aqueous solution of sulphydric acid contains about three times its volume of the gas. It is a clear colourless liquid, having a slight acid reaction, and the smell and taste of the gas. It is gradually decomposed by exposure to air, its hydrogen being oxidised into water and its sulphur set free. Sulphydric acid when burnt yields sulphurous acid, as we have seen; but when moist sulphydric acid, mixed with air or oxygen, is exposed to a moderately warm temperature, from 40° to 90°, it is converted into sulphuric acid. Sulphydric acid is recognised by the black discoloration it produces on paper moistened with solutions of lead or bismuth, and by the black tarnish it gives to silver foil.

(143) For analytical purposes the metals are divided into three primary groups, according to their behaviour with sulphuretted hydrogen and alkaline sulphydrates. The first group comprises the metals gold, platinum, tin, arsenic, antimony, bismuth, silver, lead, mercury, copper, and cadmium, all of which are precipitated from their acidified solutions by sulphydric acid. The sulphides of the first five metals are soluble, of the last six, insoluble in excess of alkaline sulphydrate. Hence, by the action of this reagent upon the precipitate produced by sulphydric acid, we divide the metals of this first group into two sub-groups. The second group comprises nickel, cobalt, iron, manganese, and zinc, the sulphides of which metals, though not precipitated from their acidified solutions by sulphydric acid, are precipitated from their neutral or nearly neutral solutions by an alkaline sulphydrate, sulphydrate of ammonia being usually selected for the purpose. The metals chromium and aluminum are also included in the second group, for though their sulphides cannot be prepared in the moist way, yet they are precipitated by sulphydrate of ammonia in the state, not of sulphides or sulphydrates, but of hydrates, sulphydric acid being evolved, thus: —

$$Al_2Cl_3 + 3NH_3H_2S + 3H_2O = Al_2H_3O_3 + 3NH_3HCl + 3H_2S.$$

The third analytical group includes the metals barium, strontium, calcium, potassium, sodium, and lithium, the sulphydrates of which are soluble in water and consequently not precipitable. The

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metal magnesium also is included in this group, for its sulphide, though insoluble or nearly so in water, is soluble in water holding ammoniacal salts, sulphydrate of ammonia for instance, in solution.

Persulphide of Hydrogen.

Symbol, H_2S_2? *Proportional number*, 66?

(144) This compound seems to be the sulphur-representative of peroxide of hydrogen, which it much resembles in its properties. It is made by gradually adding, little by little, the solution of a persulphide of alkaline earth- or alkali-metal to an excess of chlorhydric acid diluted with twice its bulk of water:—

$$Ca_2S_5 + 2HCl = 2CaCl + H_2S_2 + S_3.$$

The persulphide of hydrogen is formed without any evolution of gas, and separates as a yellowish oily fluid, heavier than water. It has the property of dissolving sulphur to a considerable extent, owing to which circumstance its composition has not been satisfactorily established. Persulphide of hydrogen has a peculiar sulphurous disagreeable odour. It produces superficial white eschars on the skin and mouth. It is insoluble in water, but soluble in ether, forming a solution which soon decomposes and deposits crystals of sulphur. It is readily inflammable, and burns with a blue flame. It is possessed of bleaching properties analogous to those of peroxide of hydrogen.

Persulphide of hydrogen is a very unstable substance, and, especially at increased temperatures, undergoes spontaneous decomposition into sulphydric acid and sulphur. By effecting this decomposition in a sealed tube, liquid sulphydric acid may be obtained, as we have seen. The stability of the persulphide is increased by the presence of moderately strong acids. Alkalies, on the other hand, promote its decomposition. Hence if, in its preparation, the chlorhydric acid be added to the alkaline persulphide, instead of the persulphide to the acid, no persulphide of hydrogen, but only sulphydric acid and sulphur will be obtained. Under the influence of catalytic agents, such as finely-divided platinum, gold, iridium, and charcoal, which effect the similar decomposition of peroxide of hydrogen into oxygen and water, persulphide of hydrogen undergoes an instantaneous decomposition into sulphur and sulphydric acid. It reduces peroxide of manganese and the oxides of silver and gold, the last two with great violence, and frequently even with ignition.

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Sulphides and Sulphydrates.

(145) Precisely as we have oxides and hydrates formed on the type of one or more atoms of water, so we have sulphides and sulphydrates derived from one or more atoms of sulphydric acid. The more or less basylous sulphides, like their corresponding oxides, may be divided into three principal classes, mon-atomic, bi-atomic, and ter-atomic, formed respectively on the types of one, two, and three atoms of sulphydric acid. The first class includes disulphides and protosulphides, with the corresponding sulphydrates. Disulphide of nickel Ni_4S, sulphide of zinc Zn_2S, and sulphydrate of sodium $HNaS$ may be taken as examples. The second class includes bisulphides, bisulphydrates, and $\frac{3}{4}$-sulphides. Bisulphide of platinum $Pt_2''S_2$, and magnetic iron pyrites Fe_3S_2, or $Fe'(Fe_2)'''S_2$, may be taken as examples. The third class includes tersulphides and sesquisulphides, with their corresponding sulphydrates. Tersulphide of bismuth $Bi_2'''S_3$, and sesquisulphide of chromium Cr_4S_3, or $(Cr_2)_2'''S_3$, may be taken as examples. It is observable that while the sesquioxides constitute a most important class of oxides, the sesquisulphides are a very unimportant class of sulphides. As a rule, they do not occur native, are scarcely salifiable, and do not result from the ordinary analytical processes which produce the other metallic sulphides with such facility. The sulphides differ much from one another in the rapidity and completeness with which they are decomposed by acids. When finely pulverised, they are all decomposed more or less perfectly by chlorhydric acid gas, but some of them are attacked very slowly by the boiling liquid acid. All salifiable sulphides, however, behave like their corresponding oxides, when decomposed by chlorhydric acid, and yield one atom of sulphydric acid for every atom of sulphur in the sulphide, thus:—

$$\begin{aligned} Fe_2' S &+ 2HCl = H_2S + 2Fe' Cl \\ Sn_2'' S_2 &+ 4HCl = 2H_2S + 2Sn'' Cl_2 \\ Sb_2'''S_3 &+ 6HCl = 3H_2S + 2Sb'''Cl_3 \end{aligned}$$

In reference to the distinction between sulphides and sulphydrates, we find that the sulphydrates of the basylous metals, lithium, sodium, potassium, calcium, strontium, barium, and magnesium, are well-defined compounds, which dissolve in water, forming colourless solutions. The solutions of the sulphydrates of magnesium and calcium are decomposed by ebullition, with evo-

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lution of sulphydric acid, thus: $MgHS + H_2O = MgHO + H_2S$. But the other sulphydrate solutions may be evaporated down, whereby they yield colourless transparent crystals of their respective sulphydrates. These basylous sulphydrates are usually made by saturating their corresponding hydrates with sulphydric gas. The dry alkaline sulphydrates, when heated to redness out of contact with air, are decomposed into sulphydric acid and metallic sulphide: $2BaHS = H_2S + Ba_2S$; but the sulphydrates of potassium and sodium require a very strong heat to effect their decomposition. The sulphides of the acid-forming metals also appear to form definite sulphydrates, corresponding to their respective oxygen-acids; but the nature of these compounds, and still more of the sulphydrates of the intermediate metals, is not well established. It is not clear, for instance, whether the so-called hydrated sulphide of zinc consists of ZnHS, or $Zn_2S . H_2O = ZnHS . ZnHO$. The hydrated sulphides of the ferric and plumbic families seem indeed not to be sulphydrates; for when soluble salts of the metals of these families are added to solutions of alkaline sulphydrate, sulphydric acid is evolved:—

$$Fe_2SO_4 + H_2O + 2KHS = K_2SO_4 + Fe_2S . H_2O + H_2S.$$

Moreover, it is not clear that all sulphides precipitated from metallic solutions by excess of sulphydric acid, or a sulphydrate, are necessarily either hydrated or sulphydrated, despite their greater solubility in acid, and their difference in colour from the undoubtedly anhydrous sulphides made in the dry way. We know, for instance, that the difference between the native scarlet sulphide of mercury and the precipitated black sulphide, or that between the native grey sulphide of antimony and the precipitated orange sulphide, is not a difference of hydration at all, but one of molecular condition, *i.e.* allotropy.

The protosulphides of the alkali- and alkaline earth-metals dissolve in water, forming colourless solutions, from which, by evaporation, the solid sulphides may, it is said, be again procured, and in the crystalline condition. It is not improbable that the solutions really contain mixtures of alkaline hydrate and sulphydrate, resulting from the reaction of the sulphide with water, thus: $K_2S + H_2O = KHS + KHO$. At any rate, precisely similar solutions are made by mixing equal quantities of alkaline hydrate and sulphydrate. With the exception of the above sulphides of the basylous metals, all sulphides and hydrated sulphides are insoluble

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in water or very nearly so. Those which, like the tersulphide of arsenic, are sparingly soluble in pure water are insoluble in acidulated water. This tersulphide, when recently precipitated, is slowly but completely decomposed by boiling with water into arsenious and sulphydric acids.

As a rule, the sulphides and oxides of the same metal have similar formulæ, and correspond in their general behaviour. Occasionally, indeed, we have metallic oxides to which there are no corresponding sulphides, the peroxide of manganese for example, and more frequently metallic sulphides to which there are no corresponding oxides, the disulphide of iron and the bisulphide of arsenic for example. Among the sulphides to which there are no corresponding oxides, perhaps the most remarkable are the alkaline polysulphides. The metal potassium, for instance, is said to form the following compounds:—

K_2S Protosulphide.
K_2S_2 Bisulphide.
K_2S_3 Tersulphide.
K_2S_4 Tetrasulphide.
K_2S_5 Pentasulphide.

When protosulphide of potassium is fused with excess of sulphur, the pentasulphide is formed as a dark liver-coloured mass which sinks beneath the excess of melted sulphur. It is a very definite compound, soluble in water, forming a deep orange liquid, which may also be obtained by boiling an excess of sulphur with a solution of the protosulphide. Its composition corresponds with that of the sulphate and thiosulphate of potassium, thus:—

$K_2S\ O_4$ Sulphate.
$K_2S_2O_3$ Thiosulphate.
K_2S_5 Pentasulphide.

It is doubtful whether the three intermediate polysulphides are other than mixtures of proto- and penta-sulphide. They may, however, be definite sulphides corresponding to the polythionic series of oxygen salts, thus:—

Bisulphide K_2S_2.	$K_2S_2O_6$ Dithionate.
Tersulphide K_2S_3.	$K_2S_3O_6$ Trithionate.
Tetrasulphide K_2S_4.	$K_2S_4O_6$ Tetrathionate.
Pentasulphide K_2S_5.	$K_2S_5O_6$ Pentathionate.

It is observable, moreover, that the three intermediate polysulphides result from definite reactions, and that the bisulphide and

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tersulphide correspond to definite oxides. The yellow colour, which solutions of alkaline protosulphide and sulphydrate acquire by exposure to air, is due to the production of polysulphides, thus: $2KHS + O = K_2S_2 + H_2O$. The yellow solutions of the polysulphides eventually become colourless by absorption of oxygen, which produces a thiosulphate, accompanied, in the case of the ter-, tetra-, and pentasulphides, with a deposit of sulphur. The polysulphides do not appear to form corresponding polysulphydrates; for when sulphur is boiled with solutions of sulphydrates, there is always an evolution of sulphydric acid, thus:—

$$2KHS + S = K_2S_2 + H_2S.$$

The distinction between neutral and salifiable sulphides is much less marked even than that between neutral and salifiable oxides. Bisulphide of iron, for instance, is obviously the representative of the non-salifiable peroxide of manganese. The two compounds, when heated in close vessels, undergo precisely similar decompositions, as we have seen:—

$$3Mn_2O_2 = 2Mn_3O_2 + O_2.$$
$$3Fe_2S_2 = 2Fe_3S_2 + S_2.$$

On the other hand, the sesquisulphide of iron is obviously the representative of the salifiable sesquioxide of that metal, and should correspond with it in its reaction with chlorhydric acid, thus:—

$$Fe_4O_3 + 6HCl = 2Fe_2Cl_3 + 3H_2O.$$
$$Fe_4S_3 + 6HCl = 2Fe_2Cl_3 + 3H_2S.$$

But sulphydric acid has the property of reducing sesquichloride of iron to the state of protochloride, with a deposition of sulphur, thus: $2Fe_2Cl_3 + H_2S = 4FeCl + 2HCl + S$. Hence the actual behaviour of sesquisulphide of iron, when treated with chlorhydric acid, corresponds, not with that of the salifiable sesquioxide of iron, but with that of the indifferent sesquioxide of cobalt:—

$$Co_4O_3 + 4HCl = 4CoCl + 2H_2O + O.$$
$$Fe_4S_3 + 4HCl = 4FeCl + 2H_2S + S.$$

The sulphides of the chlorous metals have characters corresponding to those of the corresponding metallic anhydrides; that is to say, they unite with the sulphides of the basylous metals to form corresponding soluble salts. The bisulphide of tin, and the ter- and pentasulphides of antimony and arsenic, for instance, dissolve in

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sulphydrate of potassium or ammonium, precisely as do the corresponding oxides in oxhydrate of potassium or ammonium. Thus we have stannate of potassium K_2SnO_3 or $K_2O.SnO_2$, and sulphostannate of potassium K_2SnS_3 or $K_2S.SnS_2$. When these chlorous sulphides dissolve in alkaline hydrates, they form both sulpho- and oxysalts, thus:—

$$3SnS_2 + 6KHO = 2K_2SnS_3 + K_2SnO_3 + 3H_2O.$$

(146) The sulphides frequently occur native; those of zinc, cadmium, iron, nickel, cobalt, copper, lead, mercury, silver, bismuth, antimony, arsenic, and tin, for instance. They may be prepared by very many processes. *α.* By heating the metal with sulphur. This is a method of considerable generality. In this way the sulphide of iron used for generating sulphydric acid is usually prepared. The temperature at which sulphur combines with several of the metals—zinc and iron, for instance—is considerably above its boiling point; hence, to effect a combination, the metals themselves must be strongly heated. Some heavy metallic oxides, also, when treated with excess of sulphur, give off sulphurous anhydride, and leave a pure sulphide of metal, as does arsenic; but the majority leave a mixture of sulphide and oxide. When the hydrates or carbonates of the alkali-metals are heated with sulphur, we get sulphates and polysulphides produced. Some metallic oxides, not affected by ignition with sulphur, are converted into sulphides when treated with a mixture of sulphur and alkaline carbonate. In this way, the sesquisulphides of chrome and uranium are obtained.

β. By adding sulphydric acid, or a soluble sulphydrate, to a metallic salt in solution. This method is applicable with the salts of all the ordinary heavy metals excepting chrome and aluminum: the precipitates are usually considered to be hydrated sulphides. Or, instead of treating the metallic salt in solution, we may pass sulphuretted hydrogen gas over the finely-pulverised oxides, either at ordinary or at increased temperatures, according to circumstances.

γ. Some metals, when heated in sulphydric acid gas, liberate hydrogen and form sulphides. In several metallurgic processes, sulphides are produced by heating a basylous metal, not with sulphide of hydrogen, but with the sulphide of some other metal. Thus, sulphide of iron results from the reduction of grey antimony ore with scrap iron:—

$$Fe_6 + Sb_2S_3 = Sb_2 + 3Fe_2S.$$

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δ. By reducing sulphates or other oxidised sulphur-salts. This reduction may often be effected by a current of hydrogen at a red heat. The sulphides of the alkali- and alkaline earth-metals are frequently made by igniting the sulphates with charcoal, thus: $Ba_2SO_4 + C_2 = Ba_2S + 4CO$.

ε. Sulphides may also be prepared by passing the vapour of bisulphide of carbon over metallic oxides at a red heat. In this way the sulphide of titanium is usually obtained: $TiO_2 + CS_2 = TiS_2 + CO_2$.

(147) Most of the native metallic sulphides occur in a crystalline condition. Some of them are possessed of characteristic colours, as the scarlet sulphide of mercury or cinnabar, and the yellow sulphide of arsenic or orpiment. Others of them have a highly metallic aspect, as the tersulphide of antimony or grey antimony ore, the sulphide of lead or galena, and the sulphides of iron and copper, or pyrites. Some of them are lustrous, but at the same time translucent, as is the sulphide of zinc or blende. At ordinary temperatures, all metallic sulphides occur as more or less brittle solids, though the native bisulphide of tin has a certain degree of flexibility. They undergo fusion when heated. The sulphides of the readily-fusible metals are less fusible, those of the difficultly-fusible metals more fusible, than are the corresponding metals themselves. Many metallic sulphides sublime, those of mercury and arsenic below a red heat. The sulphides of gold, platinum, and mercury are completely decomposed at a red heat, and some persulphides of other metals—iron and tin, for instance—give off a portion of their sulphur. None of the sulphides of metal can be heated to redness in the presence of air without undergoing decomposition or oxidation. When they are ignited in a current of air, we either obtain sulphates, as in the case of the sulphides of highly basylous metal, or sulphurous anhydride and metallic oxide, as in the case of the sulphides of heavy metal. With the sulphides of the noble metals, gold, platinum, silver, and mercury, however, we obtain sulphurous anhydride and reguline metal. This process of heating the sulphides in a current, or with free access of air, is largely used in metallurgy, and is known by the name of roasting. We practise it on a small scale in the laboratory, by means of a glass tube open at both ends, and held at a slight inclination to the horizon. In this the sulphide is heated, whereby a current of air is drawn through the tube, and sulphurous anhydride evolved from the upper opening. But many sulphides, and particularly hydrated sulphides, react with air at ordinary temperatures. We have already

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observed that solutions of alkaline sulphides or sulphydrates are quickly decomposed by exposure to air, yielding a deposit of sulphur, and forming thiosulphates, sulphites, and sulphates consecutively. These alkaline sulphides were employed by Scheele for eudiometrical purposes, as absorbents of the oxygen in air or other gaseous mixtures. The anhydrous protosulphides of alkali-metal, when in a fine state of division, are pyrophoric, or absorb oxygen from the air with such violence as to take fire. The sulphides of the ferric family of elements also, particularly the precipitated sulphides, are decomposed by air at ordinary temperatures. In some cases we get sulphur liberated and metallic oxide formed, with only a small quantity of sulphate; in other cases, we get the sulphate produced principally, with only a small quantity of oxide and free sulphur, thus:—

$$H_2O + 2Fe_2S + O_3 = 2HFe_2O_2 + S_2.$$
$$Cu_2S + O_4 = Cu_2SO_4.$$

Metallic sulphides, when acted on by strong nitric or nitromuriatic acid, are rapidly oxidised, forming metallic oxide or chloride, sulphuric acid, and usually some free sulphur, which melts into globules that are very difficult to oxidise. All sulphides, when heated in a current of chlorine, yield chloride of sulphur and metallic chloride. The sulphides of the more or less chlorous metals are attacked most readily. Some sulphides, when heated with hydrogen or carbon, are reduced to the metallic state, with formation of sulphydric acid, or bisulphide of carbon respectively. The reactions of the sulphides with water and acid have been already described. All sulphides, when heated with carbonate of sodium, yield a mass which, when moistened with water, gives a black stain to silver foil, and when moistened with acid gives off sulphuretted hydrogen.

Chlorides of Sulphur.

(148) In order to manifest the analogy which subsists between the hydrogen-compounds of sulphur and their chlorine derivatives, it is preferable to style these last bodies sulphides of chlorine, despite the extreme electro-negative characters of chlorine. There are, then, two well-known sulphides of chlorine, namely, the protosulphide of chlorine Cl_2S, analogous to sulphydric acid H_2S, and the bisulphide of chlorine Cl_2S_2, analogous to persulphide of hydrogen H_2S_2. There is also a questionable tetrachloride of sulphur

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SCl_4, the chloro-representative of sulphurous anhydride SO_2'', and analogue of tetrachloride. of selenium $SeCl_4$. Bromine unites directly with sulphur to form a deep red liquid, apparently the analogue of bisulphide of chlorine. It reacts with water as does the chlorine compound, and is decomposed to a very considerable extent by distillation. Iodine also unites with sulphur to form a grey, metallic-looking, semi-crystalline mass, from which alcohol extracts the whole of the iodine. The iodine of the compound is, moreover, gradually evolved by exposure to air.

(149) PROTOSULPHIDE OF CHLORINE. *Sym.* Cl_2S; *p. n.* 105; *v. d.* 52·5; □□.—This body is made by passing dry chlorine gas through persulphide of chlorine: $Cl_2S_2 + Cl_2 = 2Cl_2S$. The chlorine is rapidly absorbed, and a deep red liquid formed. The excess of chlorine is expelled by gentle ebullition. Protosulphide of chlorine has a sp. gr. 1·62. It does not solidify at − 30°. It boils at 64°, and during ebullition undergoes a partial decomposition. It evolves chlorine by exposure to sunlight. When mixed with water, it is decomposed chiefly into chlorhydric and thiosulphuric acids, which last eventually breaks up into sulphurous acid and sulphur:—

$$2Cl_2S + 3H_2O = 4HCl + H_2S_2O_3, \text{ or } H_2SO_3 + S.$$

Nitric acid converts it into chlorhydric and sulphuric acids. With ammonia it combines directly to form sulphide of chlorammonium $(NH_3Cl)_2S$, or sulphochloride of chlorammonium $(NH_3Cl)ClS$. Guthrie has shown that it combines in a somewhat similar manner with the olefines; thus with ethylene he obtained the sulphochloride of chlorethyl $C_2H_4Cl.ClS$, an analogue of mercaptan $C_2H_5.HS$, or of alcohol $C_2H_5.HO$. By gradual oxidation it yields chlorosulphurous and chlorosulphuric aldehyds, Cl_2SO and Cl_2SO_2 respectively.

(150) PERSULPHIDE OF CHLORINE. *Sym.* Cl_2S_2; *p. n.* 137; *v. d.* 63·5; □□.—This compound is procured by passing dry chlorine gas through an excess of melted sulphur, and distilling. It is a mobile yellow-red liquid, having a peculiar unpleasant penetrating smell, and fuming strongly in the air. Its sp. gr. is 1·687. It boils at 139°. When dropped into water it sinks in the form of oily drops, and is slowly decomposed into chlorhydric acid, sulphur, and thiosulphuric acid, which last gradually decomposes into sulphurous acid and sulphur:—

$$2Cl_2S_2 + 3H_2O = 4HCl + S_2 + H_2S_2O_3, \text{ or } H_2SO_3 + S.$$

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It combines directly with ammonia to form bisulphide of chlorammonium $(NH_3Cl)_2S_2$, and with ethylene to form bisulphide of chlorethyl $(C_2H_4Cl)_2S_2$. It dissolves sulphur in large quantities, especially when heated. It constitutes, when saturated with sulphur at ordinary temperatures, a clear yellow liquid, of sp. gr. 1·7, and containing altogether 66·7 per cent. of sulphur. The solution, in crude benzene, of bisulphide of chlorine with excess of sulphur, is used for vulcanising or sulphurising india-rubber.

(151) TETRACHLORIDE OF SULPHUR. *Sym.* SCl_4; *p. n.* 174.—This compound has never been isolated. When chlorine gas is passed over certain metallic sulphides—those of tin and antimony, for instance—a double chloride of metal and sulphur is produced, in which the constituent chloride of sulphur has a composition represented by the formula SCl_4. By saturating protochloride of sulphur with chlorine, at very low temperatures, Carius obtained a body having a composition almost exactly intermediate between that of protosulphide of chlorine and that of tetrachloride of sulphur, probably a mixture of the two.

OXIDISED COMPOUNDS OF SULPHUR.

(152) A complete series of oxidised compounds of sulphydric acid should comprise the following members, corresponding to the oxides of chlorhydric acid:—

Sulphydric acid	H_2S	HCl	Chlorhydric acid.
———	H_2SO	HClO	Hypochlorous acid.
———	H_2SO_2	$HClO_2$	Chlorous acid.
Sulphurous acid	H_2SO_3	$HClO_3$	Chloric acid.
Sulphuric acid	H_2SO_4	$HClO_4$	Perchloric acid.

The chlorine acids are monobasic, or contain but one atom; the sulphur acids are bibasic, or contain two atoms of hydrogen replaceable by metal. Thus sulphurous acid forms neutral sulphites M_2SO_3, and acid sulphites $MHSO_3$. Sulphuric acid forms neutral sulphates M_2SO_4, and acid sulphates $MHSO_4$. Both acids, moreover, form double salts, in which each atom of hydrogen is displaced by a different metal, potassio-sulphate of nickel $KNiSO_4$, for example.

The first and second members of the sulphur series of oxygen compounds are at present unknown to us, but we are acquainted with their chloro-derivatives, namely sulphuric chloraldehyd Cl_2SO_2, and sulphurous chloraldehyd Cl_2SO; oxidised compounds

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of chloride of sulphur Cl_2S, the chloro-representative of sulphydric acid.

The formulæ of the sulphurous and sulphuric acids, and of bibasic acids generally, may be written so as to indicate their separation into water and anhydride, thus:—

	Anhydrides.	Acids.
Sulphurous	SO_2	$H_2SO_3 = H_2O . SO_2$
Sulphuric	SO_3	$H_2SO_4 = H_2O . SO_3$.

The acids, when acted upon by different re-agents, break up in a variety of ways, each of which might be indicated by breaking the formulæ in a different manner; but practically the above broken formulæ are the only ones generally useful, inasmuch as the above mode of breaking up into water and anhydride is the only one of very frequent occurrence.*

Sulphurous and sulphuric acids can be formed from the anhydrides by direct hydration, and the anhydrides from the acids by direct dehydration.

Sulphurous and sulphuric acids can both be obtained by the direct oxidation of sulphydric acid; and reversely, metallic sulphides can be obtained by the deoxidation of sulphites and sulphates. Sulphurous acid, moreover, very readily affords sulphydric acid by deoxidation.

Sulphurous and sulphuric acids are convertible into one another by oxidation and deoxidation respectively.

The sulphurous and sulphuric chloraldehyds yield sulphurous and sulphuric acids respectively by treatment with water, and may be re-formed from these acids respectively by acting on them with pentachloride of phosphorus. They may also be produced from chloride of sulphur, as previously alluded to.

Allied to the sulphates we have a group of salts known as the thiosulphates, or more frequently by the unsystematic name of hyposulphites. They seem to be sulphates in which one of oxygen is replaced by an atom of sulphur, as shown by their formulæ. Thus Na_2SO_4 = sulphate of sodium, $Na_2S(O_3S)$, or $Na_2S_2O_3$ = hyposulphite or thiosulphate of sodium. When a sulphite Na_2SO_3 is acted upon by oxygen or a peroxidised substance, it becomes an oxisulphate; when it is acted upon by sulphur or a persulphuretted substance, it becomes a thiosulphate. We have before alluded to

* The following formulæ for sulphuric acid represent other modes in which the acid may be broken up: $H_2.SO_4$, $H_2S.O_4$, $H_2O_2.SO_2$, &c.

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the partial or complete displacement of oxygen by sulphur in salts.

We have also a remarkable series of acids with six atoms of oxygen and two or more atoms of sulphur. They constitute the polythionic series, and are represented by the following formulæ:—

$H_2S_2O_6$ Dithionic acid.
$H_2S_3O_6$ Trithionic acid.
$H_2S_4O_6$ Tetrathionic acid.
$H_2S_5O_6$ Pentathionic acid.

The dithionates are made directly from sulphurous anhydride and a metallic peroxide, thus: $Mn_2O_2 + 2SO_2 = Mn_2S_2O_6$. When heated, they break up into a sulphate and sulphurous anhydride, thus: $Mn_2S_2O_6 = Mn_2SO_4 + SO_2$. The tri-, tetra-, and pentathionates undergo a similar decomposition when heated, but yield sulphur in addition.

SULPHUROUS ALDEHYD; H_2SO, *wanting.*

(153) SULPHUROUS CHLORALDEHYD. *Sym.* Cl_2SO; *p. n.* 119.—This compound, also known as chloride of thionyl $(SO)''Cl_2$, results from the oxidation of both sulphides of chlorine. It is prepared, however, by the action of pentachloride of phosphorus on sulphurous anhydride, or by the action of oxichloride of phosphorus on a metallic sulphite:—

$$SO_2 + Cl_5P = Cl_2SO + Cl_3PO.$$
$$3Ca_2SO_3 + 2Cl_3PO = 3Cl_2SO + 2Ca_3PO_4.$$

It is separated by distillation from the fixed phosphate of calcium produced simultaneously in the second, and by fractional distillation from the volatile phosphoric chloraldehyd produced simultaneously in the first reaction. It is a colourless highly refractive liquid, boiling at 82°. It is decomposed by water, alcohol, ammonia, &c., after the manner of chloraldehyds in general, forming sulphurous acid, ethylsulphurous acid, and thionamide respectively. Sulphurous chloraldehyd, sulphurous acid, and thionamide may be represented on the double types chloride, hydrate, and amide, respectively, as follows:—

$$(SO)''Cl_2 = Cl_2SO, \qquad \left.\begin{matrix}(SO)''\\H_2\end{matrix}\right\}O_2 = (HO)_2SO, \qquad \left.\begin{matrix}(SO)''\\H_2\\H_2\end{matrix}\right\}N_2 = (NH_2)_2SO.$$

SULPHURIC ALDEHYD; H_2SO_2, *wanting.*

(154) SULPHURIC CHLORALDEHYD. *Sym.* Cl_2SO_2; *p. n.* 135; *v. d.* 62·5; □□. This compound, also known as chloride of

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sulphuryl $(SO_2)''Cl_2$, results from the direct combination of dry chlorine with sulphurous anhydride under the influence of sunlight. Similar bodies may be formed by the action of bromine and iodine upon sulphurous anhydride, but all three direct combinations take place very sluggishly and imperfectly. Sulphuric chloraldehyd may also be made by the action of pentachloride of phosphorus on sulphuric anhydride; but it is best obtained by treating sulphuric acid with the pentachloride, or sulphate of lead with the oxichloride of phosphorus, and distilling:—

$$SO_3 + Cl_5P = Cl_2SO_2 + Cl_3PO.$$
$$H_2SO_4 + 2Cl_5P = Cl_2SO_2 + 2Cl_3PO + 2HCl.$$
$$3Pb_2SO_4 + 2Cl_3PO = 3Cl_2SO_2 + 2Pb_3PO_4.$$

Sulphuric chloraldehyd is a colourless fuming liquid of sp. gr. 1·66. It boils at 77°, and may be distilled unchanged over caustic lime or baryta. When poured into water, it sinks in the form of oily drops, which gradually disappear, being converted into sulphuric and chlorhydric acids:—

$$Cl_2SO_2 + 2HHO = 2HCl + (HO)_2SO_2 \text{ or } H_2SO_4.$$

With alcohol it behaves in a similar manner, thus:—

$$Cl_2SO_2 + 2C_2H_5HO = 2C_2H_5Cl + (HO)_2SO_2 \text{ or } H_2SO_4.$$

In the actual reaction, the sulphuric acid appears in the form of ethylsulphuric acid, through the intervention of another atom of alcohol:—

$$C_2H_5HO + H_2SO_4 = HHO + C_2H_5HSO_4$$

By its action upon dry ammonia, or upon the commercial sesquicarbonate of ammonia, it produces sulphamide:—

$$4NH_3 + Cl_2SO_2 = 2NH_3HCl + (NH_2)_2SO_2 \text{ or } N_2H_4SO_2.$$

Sulphuric chloraldehyd, sulphuric acid, and sulphamide may be represented on the double types chloride, hydrate, and amide respectively, as follows:—

$$(SO_2)''Cl_2=Cl_2SO_2, \quad \left.\begin{matrix}(SO_2)''\\H_2\end{matrix}\right\}O_2=(HO)_2SO_2, \quad \left.\begin{matrix}(SO_2)''\\H_2\\H_2\end{matrix}\right\}N_2=(NH_2)_2SO_2.$$

A third oxichloride of sulphur results from the transmission of moist chlorine through protosulphide of chlorine. It occurs as a crystalline body, which is decomposed by water into chlorhydric and sulphuric acids.

(155) Chlorhydrosulphurous Acid. *Sym.* $HClSO_3$; *p. n.*

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116·5.—This interesting body, which may be regarded as a chloro-derivative of the compound next to be considered, namely, sulphurous acid H_2SO_3, was first defined, if not discovered, by Williamson, who, moreover, deduced from its formation certain most important theoretical considerations. By the agency of pentachloride of phosphorus, a monatomic oxacid is converted into its corresponding chloraldehyd by an exchange of peroxide of hydrogen for chlorine; and, conversely, by the agency of water, a monatomic chloraldehyd is converted into its corresponding acid by an exchange of chlorine for peroxide of hydrogen. Thus we have nitric chloraldehyd NO_2Cl, and nitric acid NO_2HO, mutually convertible into one another as above described. The ultimate results of the action of pentachloride of phosphorus upon diatomic sulphuric acid, and of water upon diatomic sulphuric chloraldehyd, correspond with the above conversions, as we have already seen; but whereas the mutual conversion of the chloride and hydrate of nitryl admits only of one stage, that of the bichloride and bihydrate of sulphuryl admits of two stages. Thus we have—

$$Cl_2SO_2 \text{ or } \left.\begin{matrix}Cl\\Cl\end{matrix}\right\}SO_2, \quad \text{and } HClSO_3 \text{ or } \left.\begin{matrix}Cl\\HO\end{matrix}\right\}SO_2, \quad \text{and } H_2SO_4 \text{ or } \left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2.$$

This intermediate compound is the body now under consideration. It results from the action of moisture upon chlorosulphuric aldehyd, thus:—

$$Cl_2SO_2 + HHO = Cl(HO)SO_2 + HCl.$$

It also constitutes the first product of the action of pentachloride of phosphorus upon sulphuric acid, thus;—

$$(HO)_2SO_2 + Cl_5P = Cl(HO)SO_2 + HCl + Cl_3PO.$$

This, which is Williamson's original reaction, furnishes the most ready means of preparing the compound. Rose obtained it by distilling a mixture of protosulphide of chlorine and Nordhausen sulphuric acid. It may also be procured by the direct combination of chlorhydric acid and sulphuric anhydride, and by the action of platinum black upon an imperfectly dried mixture of chlorine and sulphurous anhydride.

Chlorhydrosulphurous acid is a colourless liquid, boiling at 145°, and simultaneously undergoing a partial decomposition into sulphuric acid and sulphuric chloraldehyd. With pentachloride of phosphorus it forms sulphuric chloraldehyd. When poured into water, it sinks to the bottom, and gradually dissolves, with formation of sulphuric and chlorhydric acids. It has decided acid pro-

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perties, and forms definite salts, in which its hydrogen is replaced by metal. It dissolves chloride of sodium at a gentle heat, with evolution of chlorhydric acid and formation of chlorosulphite of sodium $NaClSO_3$. It reacts with nitrate of sodium to form acid sulphate of sodium and chloride of nitryl:—

$$Na(NO_2)O + HClSO_3 = HNaSO_4 + NO_2Cl.$$

The formation of intermediate compounds, analogous to chlorosulphurous acid, is characteristic of the biatomic acids and chloraldehyds in general.

Sulphurous Anhydride, Acid, and Salts.

(156) When sulphurous anhydride SO_2, is received into water H_2O, the combination of the two to form sulphurous acid H_2SO_3, is attended with considerable evolution of heat. Moreover, the compound H_2SO_3 has been actually isolated by Döpping in the form of cubical crystals. On the other hand, when a solution of sulphurous acid is boiled, and the vapour passed over ordinary desiccating agents, such as chloride of calcium, oil of vitriol, &c., we obtain at once the simple dry anhydride. The salts of sulphurous acid, M_2SO_3 and $MHSO_3$, are very well defined compounds. Sulphurous acid or anhydride occurs in volcanic neighbourhoods in the gaseous state, and dissolved in the water of the springs.

(157) Sulphurous Anhydride. *Sym.* SO_2; *p. n.* 64; *v. d.* 32; □□.—*a.* Oxidation process. This gas may be made by igniting sulphur in dry oxygen. The sulphur burns with a violet flame, and the resulting gas, after cooling, is found to occupy exactly the bulk of the original oxygen. Sulphurous anhydride also results from burning sulphur in the air, from roasting metallic sulphides, and from heating sulphur with metallic oxides, those of copper and manganese for instance.

β. De-oxidation process. Sulphurous anhydride is usually obtained by deoxidating sulphuric acid. In the laboratory we boil the acid with metallic mercury or copper: the reaction is:—

$$\left.\begin{matrix} Hg_2 \\ Cu_4 \end{matrix}\right\} + 2H_2SO_4 = \left.\begin{matrix} Hg_2 \\ Cu_4 \end{matrix}\right\} SO_4 + 2H_2O + SO_2.$$

In the case of mercury, we get a protosulphate, in the case of copper a di-sulphate of metal. According to Mauméné, sulphide

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and disulphide of copper are also formed. The gas may be passed through a small quantity of water to wash it, and may then be dried over chloride of calcium. In the manufactory, we find charcoal, straw, sawdust, &c., substituted for the metals, but the sulphurous anhydride obtained by means of these substances is always contaminated with about half its bulk of carbonic anhydride. Wach recommends a laboratory process for making sulphurous anhydride, by heating sulphur and sulphuric anhydride together in sealed V-tubes, whereby the anhydride is obtained in the liquid state, at the cooled extremity.

At common temperatures, sulphurous anhydride is a gas, but it may very readily be condensed into the liquid state by a pressure of three atmospheres, or by a freezing mixture of ice and salt. The liquid anhydride may be obtained in large quantities by heating copper turnings with sulphuric acid, and passing the evolved gas first through a little water to wash it, then through an empty U-tube surrounded by ice to cool the gas and condense its moisture, then through a chloride of calcium tube to render it perfectly dry, and lastly into a suitable receiver immersed in a freezing mixture of salt and ice. The product thus obtained may be preserved in sealed tubes, or in soda-water bottles firmly corked and wired, or preferably closed with a vulcanised caoutchouc pad retained by a screw-clamp. When the liquid anhydride is evaporated rapidly under the air-pump, or when it is cooled by a mixture of sold carbonic anhydride and ether, it solidifies in white semi-crystalline flakes. The solid anhydride is heavier than the liquid. It melts at about $-79°$. The liquid anhydride is a colourless, transparent, mobile fluid. Its specific gravity is 1·45. It boils at $-10°$. By its evaporation it produces intense cold, sometimes even sufficient to freeze itself, and readily to freeze water on which it is poured. The gaseous anhydride is colourless, irrespirable, and incombustible. It rapidly extinguishes the flame of burning bodies. It is more than twice as heavy as atmospheric air, and may consequently be collected by displacement. It may also be collected over mercury, but not over water, in which it is very soluble. It has a peculiar suffocating sulphurous odour. When perfectly dry, it does not redden litmus paper, at any rate, not for some time. It temporarily bleaches many vegetable colours. The anhydride or acid is largely used for bleaching wool, straw, &c., and for preserving certain animal tissues such as vellum and catgut. The moist substances are placed in close chambers in which sulphur is burnt. The colouring matters seem merely to enter into combination with

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the acid or anhydride, and may be reproduced by the addition of an alkali to neutralise, or of a stronger acid to expel the sulphurous. The fume of burning sulphur has also been employed as a disinfecting agent.

(158) SULPHUROUS ACID. *Sym.* H_2SO_3; *p. n.* 82.—*a.* This acid may be obtained by burning sulphydric acid in excess of air or oxygen; or by liberating it from its salts, the sulphites, by the addition of a stronger acid, such as the sulphuric, chlorhydric, oxalic, &c. *β.* In practice it is always made by passing sulphurous anhydride into water. When liquid sulphurous anhydride is added to ice-cold water, or even to ice, a combination attended by violent ebullition of the anhydride takes place, while a solid hydrated acid remains, mixed with an excess of ice, whether used as such or frozen during the reaction. The solid hydrated acid, in the form of white laminated crystals, may also be made by passing moist sulphurous anhydride-gas through a freezing mixture. Pierre obtained nitre-like crystals of sulphurous acid having the formula $H_2SO_3 . 8H_2O$, by cooling to $-6°$ a saturated solution of sulphurous acid through which a current of the gas was being transmitted. The crystals fused at $+4°$. Döpping succeeded in procuring the pure acid H_2SO_3, in the form of cubical crystals, by cooling to zero a saturated aqueous solution of sulphurous acid.

The solution of sulphurous acid is made commercially by condensing the vapour from burning sulphur in a coke scrubber through which water is kept trickling. In the laboratory the gaseous anhydride is passed into distilled water, which absorbs about 43·5 times its volume of the gas. The combination is attended by a slight elevation of temperature. The resulting liquid has a specific gravity of 1·04. It is colourless, has the smell of burning sulphur, and reacts strongly acid to test paper. When boiled, it gives off sulphurous acid or anhydride, but very prolonged ebullition is required to drive off the whole of the gas. By exposure to air, the solution slowly oxidises into sulphuric acid. When mixed with chlorhydric acid and metallic zinc or stannous chloride, it is reduced to the state of sulphydric acid, which in the case of the zinc may be recognised by its reaction on lead-paper. With stannous chloride we obtain a precipitate of brown sulphide of tin.

Both sulphurous anhydride and acid act as powerful reducing agents. They liberate iodine from iodic acid, and, in the presence of water, finally convert it into iodhydric acid. Sulphurous acid

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and iodine, in presence of a large quantity of water, yield iodhydric and sulphuric acids: $H_2SO_3 + I_2 + H_2O = 2HI + H_2SO_4$. Bunsen's method of volumetric analysis is based upon this reaction. Sulphurous acid and anhydride reduce the arsenic, chromic, and permanganic acids, and precipitate metallic gold from its chloride. They also precipitate tellurium and selenium from tellurous and selenious acids respectively.

(159) SULPHITES. *Sym.* $MHSO_3$ *acid salt;* M_2SO_3 *normal salt.* —*a.* These salts are usually made by transmitting sulphurous gas through water in which metallic hydrates or carbonates are dissolved or suspended. The acid sulphites of barium, strontium, calcium and magnesium, and the neutral and acid sulphites of lithium, sodium, and potassium are soluble in water. *β.* Most other sulphites are insoluble, and may be prepared by precipitation with a sulphite of alkali-metal. The sulphites M_2SO_3 and $MHSO_3$, present a great analogy to, and are for the most part isomorphous with, a class of salts we shall subsequently have to consider, namely, the carbonates, M_2CO_3 and $MHCO_3$ respectively. Both acid and neutral salts form well-defined crystals, sometimes hydrated, most generally anhydrous. The sulphites are decomposed at a red heat, either into sulphate and sulphide, or into sulphurous anhydride and metallic oxide. When heated with charcoal, they are completely reduced to the state of sulphides, or in some cases to that of oxides. They are also readily reduced in the moist way by stannous chloride, or by nascent hydrogen evolved from chlorhydric acid and zinc, with formation of metallic sulphide or of sulphydric acid. The sulphites, particularly if in solution, become converted into sulphates, by exposure to air, or by treatment with oxidising agents, such as nitrous acid, hypochlorous acid, chlorine, &c. The solutions, also, when acted on by sulphur, sulphydric acid, or alkaline sulphydrate, form thiosulphates, *i. e.* hyposulphites. The sulphites are decomposed by nearly all acids, save the carbonic and boric, with liberation of sulphurous acid. The acidified solutions of the salts act like sulphurous acid as powerful reducing agents, and are frequently employed as such in analysis. Acid-sulphite of sodium was at one time much used as an *antichlore.*

SULPHURIC ANHYDRIDE, ACID, AND SALTS.

(160) The distinctions between sulphuric acid and anhydride, unlike those between sulphurous acid and anhydride, are extremely marked. Moreover, each of the bodies is procurable in a

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well-defined state. Sulphuric anhydride SO_3, reacts violently with water to form the acid H_2SO_4; and the acid by de-hydration readily yields the anhydride. It appears also, from the experiments of Marignac, that sulphuric acid, when boiled, is partially decomposed into water and anhydride; or, in other words, it undergoes to some extent the same kind of decomposition that sulphurous acid undergoes so completely.

(161) SULPHURIC ANHYDRIDE. *Sym.* SO_3; *p.n.* 80; *v.d.* 40; □□.

a. This compound may be obtained by passing dried sulphurous anhydride and oxygen or air over certain metallic oxides heated to dull redness, thus: $SO_2 + O = SO_3$. A mixture of cupric and chromic oxides is found to be most efficacious in practice. Platinum-foil and spongy platinum induce the same combination of the two gases at a temperature considerably below redness.

β. It may also be prepared in large quantities by heating sulphuric acid with phosphoric anhydride, thus: $H_2SO_4 - H_2O = SO_3$. The fixed phosphoric anhydride abstracts water from the sulphuric acid, and the volatile sulphuric anhydride distils over and condenses as a white crystalline solid.

γ. By igniting certain persulphates, such as those of iron, antimony, &c., there distils over a mixture or combination of sulphuric acid and anhydride. By heating this distillate in a retort, the volatile anhydride is readily driven off from the comparatively fixed acid. Nordhausen oil of vitriol, which appears to be a definite compound, $H_2SO_4 . SO_3$, is thus decomposed by heat into acid and anhydride. In a similar manner, the anhydro-sulphate of sodium $Na_2SO_4.SO_3$, formed by heating the acid-sulphate $NaHSO_4$, nearly to redness, breaks up, when more strongly heated, into sulphate of sodium and sulphuric anhydride.

At ordinary temperatures, the anhydride occurs as a white crystalline, fibrous or asbestus-like mass, having a specific gravity 1·95. It fuses at 24·5° into a colourless or slightly brown (from a trace of organic matter) and almost oily liquid, having a specific gravity, 1·97. It boils at 52·6°. The solid anhydride is somewhat tough and difficult to cut. It may be moulded in the dry fingers without inconvenience, until by its deliquescence it is partly converted into sulphuric acid. It gives off opaque white fumes in the air, especially in moist air. It does not redden dry litmus paper. It has a great tendency to unite with water, and by its abstraction thereof soon chars wood, paper, sugar, &c. It hisses violently when thrown into water, thereby becoming sulphuric acid. The vapour, when passed through a red-

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hot tube, is resolved into a mixture of one volume of oxygen with two volumes of sulphurous anhydride. Phosphorus takes fire when heated in the vapour, unites with the oxygen, and liberates sulphur. Mercury, when gently heated with the anhydride, becomes mercuric sulphate, and sets free sulphurous anhydride. Sulphuric anhydride dissolves sulphur to form several more or less definite compounds of a brown, green, and blue colour respectively. The presence of a small quantity of sulphuric acid seems essential to the production of these compounds. The dry anhydride dissolves, and forms a crystalline compound of a green colour with iodine. It also produces a crystalline compound with nitric oxide gas, and absorbs sulphurous anhydride to form a thin liquid having probably the composition $SO_2 . 2SO_3$. When vapour of sulphuric anhydride is passed over anhydrous baryta, at a moderate heat, combination takes place, accompanied with vivid incandescence, and production of sulphate of barium $Ba_2O . SO_3$, or Ba_2SO_4.

(162) SULPHURIC ACID. *Sym.* H_2SO_4; *p. n.* 98; *v. d.* 24·5; ⊞.

a. This acid, as we have already seen, may be obtained by the hydration of the anhydride, by the decomposition of sulphuric chloraldehyd with water, by the oxidation of moist sulphydric acid in warm air, by the oxidation of sulphur with nitromuriatic acid, &c., and by the decomposition of the polythionic acids.

β. By the dry distillation of metallic per-sulphates. We have before observed that the sesqui- and ter-sulphates, owing to the almost invariable presence of moisture, yield by distillation sulphuric acid as well as sulphuric anhydride. At Nordhausen, in Saxony, a sulphate of iron, consisting chiefly of per-sulphate, is dried at a moderate heat, and then distilled in earthen retorts. The distillate is received in a small quantity of water, or more frequently in concentrated sulphuric acid made by the process next to be described. A heavy brown, oily, fuming liquid is thus obtained, having a specific gravity 1·9, and corresponding pretty uniformly in its composition with the formula $H_2SO_4 . SO_3$. This acid, which seems to be a definite compound, is known as Nordhausen, or Saxon, or fuming oil of vitriol. It is chiefly used for dissolving indigo. It solidifies at zero, forming colourless transparent crystals. When gently heated, it breaks up into sulphuric anhydride which distils over, and sulphuric acid which remains. There are a few tolerably well defined salts, known as the anhydrosulphates, formed on the same type, and having for their general formula $M_2SO_4 . SO_3$ or $M_2S_2O_7$.

γ. By the oxidation of sulphurous acid. Sulphuric acid results

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from passing moist sulphurous acid and air through tubes filled with spongy platinum heated to low redness. We have seen also that sulphurous acid slowly passes into sulphuric acid by mere exposure to air, and is immediately converted thereinto by treatment with oxidising agents. The enormous quantities of sulphuric acid produced in this country, more than 100,000 tons annually, are made by burning sulphur or roasting pyrites, and oxidising the resultant sulphurous vapours by means of moist air and certain oxides of nitrogen. Sometimes, though rarely, sulphydric acid gas, produced in some other manufacturing operation, is burnt instead of or conjointly with sulphur, and the resulting sulphurous acid oxidated as above. The deutoxide of nitrogen or nitric oxide N_2O_2, which plays so important a part in the manufacture of sulphuric acid, is a colourless permanent gas, insoluble in water. In the presence of air, it absorbs oxygen instantaneously to form pernitric oxide N_2O_4, a deep orange-coloured vapour absorbable by water. Sulphurous anhydride unites directly with pernitric oxide to form a crystalline compound which, by the action of water, is immediately decomposed into sulphuric acid and nitric oxide gas. The formation of this compound is not a necessary stage in the process, and does not occur at all in the present mode of making the acid, where steam is introduced largely into the vessel or chamber in which the reaction takes place: —

$$N_2O_4 + 2SO_2 + 2H_2O = N_2O_2 + 2H_2SO_4.$$

The liberated nitric oxide again absorbs oxygen to form pernitric oxide, which again oxidises the moist sulphurous vapours into sulphuric acid, with re-liberation of nitric oxide; and so on continuously. Theoretically, a small quantity of nitric oxide should suffice to produce an indefinitely large amount of sulphuric acid.

The exact nature of the changes which nitric oxide, sulphurous anhydride, oxygen, and steam undergo in the presence of one another, has been minutely studied by several chemists, particularly by Provostaye and Dessains, but without any conclusive results being arrived at. The description given above must be considered as a general rather than a strictly accurate account of the reaction.

In the manufacture of sulphuric acid on a large scale, sulphur is burnt slowly on an iron plate forming the floor of a sort of furnace. The amount of air admitted to the sulphur is regulated by means of a smaller iron plate forming the door of the furnace,

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so that the sulphur when once ignited may go on burning, and producing sulphurous anhydride, with tolerable uniformity. Upon the iron plate on which the sulphur is burnt is also placed an iron pot containing a mixture of nitrate of sodium and sulphuric acid, which continues to generate nitric acid for some time. The sulphurous anhydride and nitric acid vapour, from one or several furnaces, are conveyed by means of flues into a large leaden chamber having a capacity of from 50 to 100 thousand cubic feet, or more. Within this chamber, into which steam is admitted continuously by several jets, the reaction chiefly occurs. The nitric acid is soon reduced to nitric oxide, after which, the succession of changes, that has been already pointed out, takes place; and dilute sulphuric acid collects on the floor of the chamber, whence it is drawn off into leaden evaporating pans. The vapours escaping from the large chamber are usually passed into one or two smaller subsidiary chambers also supplied with steam. In these, a further condensation occurs, and a still weaker acid is produced, which is run back into the large chamber to become more concentrated. In some manufactories the vapours from the subsidiary chambers are then passed through coke scrubbers, that is, through columns packed with coke over which water is constantly pouring; and here a further condensation occurs, and a very dilute acid is produced, which is pumped up into the subsidiary leaden chambers. In a few factories, Gay-Lussac's scrubber is used instead of the water scrubber. The coke in this case is kept moistened with concentrated sulphuric acid, which completely absorbs the nitric oxide gas. The acid is then pumped into a second similar scrubber, in which it is robbed of its nitric oxide by means of the sulphurous anhydride proceeding from the burning sulphur. In a theoretically perfect operation, there should be no final escape into the atmosphere of any other gas than the nitrogen of the air admitted into the furnace and thence into the chamber, but in practice a small quantity of sulphurous or nitrous gas, or both, escapes condensation, although the amount of sulphuric acid finally produced usually approximates very closely to the theoretical quantity. The acid withdrawn from the leaden chambers has generally a specific gravity about 1·55. By evaporation in a series of shallow leaden pans its specific gravity is raised to above 1·7. This acid is usually dark coloured from the presence of organic matter, and is technically known by the name of "brown acid." The further concentration has to be effected in retorts of glass or platinum. With glass retorts the operation is intermittent. A

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number of large glass retorts are heated on a sand bath until the requisite concentration is attained. Throughout the process, a diluted sulphuric acid, containing sulphurous acid from the reaction of the organic matter and sulphuric acid, distils over. This is returned to the leaden chamber, and the concentrated colourless acid siphoned off from the retorts into carboys. With a platinum retort the process is continuous. Brown acid is constantly admitted at the top, concentrated acid withdrawn from the bottom, and diluted sulphuric acid, with sulphurous acid, distilled off into receivers, whence it is pumped back into the chambers. In commerce, the concentrated colourless acid, having a specific gravity reaching to 1·842, or approximating very closely thereto, is alone known by the name of "oil of vitriol." The process above described is substantially the same as that introduced by Dr. Roebuck about the year 1720. It is known as the English mode of manufacture, and the product is called English oil of vitriol. This oil of vitriol always contains lead, and not unfrequently other impurities, chiefly arsenic and nitrous or nitric acid. By diluting it with water, the lead is thrown down as a white precipitate, which becomes black by the action of sulphuretted hydrogen. The arsenic may be recognised by Reinsch's or Marsh's tests, or by neutralising the diluted acid with carbonate of potassium, filtering from the resulting sulphate of potassium, and treating the acidulated filtrate with sulphuretted hydrogen, when a yellow precipitate will be produced. The nitrous or nitric acid can be detected by pouring in a dilute solution of sulphate of iron, so as to float on the top of the acid. Where the two fluids meet, a brownish purple ring of discoloration will be produced. The addition of sulphide of barium to arsenical sulphuric acid produces a precipitate of mixed sulphide of arsenic and sulphate of barium, which may be separated by subsidence and decantation. The acid may be purified in another way by heating it nearly to the boiling point, and passing a current of chlorhydric acid gas through it; whereby the arsenic is carried over as the volatile chloride of arsenic, while the nitric and nitrous acids are expelled almost completely. The nitrous or nitric acid may also be entirely decomposed into water and nitrogen gas, by heating the acid with a little sulphate of ammonia; and lastly, by distilling the sulphuric acid, after the separation of the arsenic and nitrous acid, it may be obtained quite pure. The distillation must be effected in large retorts, heated, not at the bottom, but somewhat at the sides, to avoid the violent percussive ebullition which results from directly heating the deposit of sul-

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phate of lead that gradually forms at the bottom of the retort. The vapour of oil of vitriol has a very small latent heat, and, under any circumstances, the ebullition of the acid is somewhat percussive. It is found that the presence of platinum clippings in the retort prevents this action to a considerable extent.

(163) Pure oil of vitriol, or normal sulphuric acid H_2SO_4, is a heavy, oily, colourless, inodorous liquid, having a specific gravity of 1·842. It boils at 327° and freezes at −35° It is very hygrometric, and, when exposed to moist air, will even double its weight in the course of a few days. Hence it is in constant requisition as a desiccating agent It abstracts water from many organic substances and thereby gives origin to new compounds. Thus alcohol, acetone, formic acid, glycerine, &c., when dehydrated by sulphuric acid, produce olefiant gas, mesitylene, carbonic oxide, and acroleine respectively. In many cases, the organic substances acted upon by sulphuric acid are completely broken up or destroyed; as is especially the case with woody fibre, sugar, and bodies of allied composition, which, by the loss of water, become thoroughly charred or carbonised. This charring effect of strong sulphuric acid is highly characteristic. The diluted acid slowly destroys organic fibres, without charring them. But tissues, moistened with dilute sulphuric acid and then heated, become charred from the concentration of the acid which gradually takes place. The admixture of the strong acid with water is attended by a great development of heat. On mixing four parts by weight of oil of vitriol with one part of water, the temperature rises from 0° to 100°. The cooled mixture of water and acid occupies a volume considerably less than that of the two separate liquids. Sulphuric acid is reduced to sulphydric acid by passing its vapour with excess of hydrogen through a tube heated to redness. Phosphorus takes fire in sulphuric acid vapour and liberates sulphur. At increased temperatures, not only zinc, iron, copper, mercury, silver, and most of the metals, save gold and platinum, but also charcoal and sulphur, exert a reducing action upon strong sulphuric acid, and evolve sulphurous acid. All the metals of the zincic and ferric families, with the exception of copper, readily displace hydrogen from the diluted acid to form their respective sulphates of metal. At ordinary, or somewhat increased temperatures, sulphuric acid decomposes nearly all the salts of other acids, with production of the corresponding sulphates and liberation of the respective acids. By its action on certain highly oxidised metallic compounds, such as the peroxides of lead and manganese, and the manganic, chromic,

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and ferric acids, or their salts, it produces sulphates of the respective metals, with evolution of oxygen gas. Sulphuric acid, like the anhydride, absorbs nitric oxide gas, to form the crystalline compound previously referred to, which dissolves unchanged in an excess of acid. The vapour of sulphuric acid is decomposed, at a red heat, into water, sulphurous anhydride, and oxygen.

Sulphuric acid reacts with a large number of hydrogenised bodies, alkaline, neutral, and acid, to form new compounds by the elimination of water. The typical reactions are the following:—

$$\text{I}^{\circ}.\quad H_2SO_4 + 2A - 2H_2O = X.$$

In accordance with this reaction, sulphamide, sulphanilide, sulphate of ethyl, sulphate of phenyl, sulphobenzide, and sulphonaphthalide, for example, are formed by the action of sulphuric acid upon ammonia, aniline, alcohol, phenol, benzene, and naphthalene, respectively. All these products are neutral in their properties.

$$\text{II}^{\circ}.\quad H_2SO_4 + A - H_2O^{*} = Y.$$

In accordance with this reaction, sulphamic acid, sulphanilic acid, sulphethylic acid, sulphophenylic acid, sulphobenzidic acid, and sulphonaphthalic acid, for example, are formed by the action of sulphuric acid upon ammonia, aniline, alcohol, phenol, benzene, and naphthalene, respectively. All these products have the properties of monobasic acids. Sulphuric acid also reacts, in accordance with the above equation, upon benzoic and other monobasic acids, but then the products of its action, sulphobenzoic acid, for instance, have the properties of bibasic acids. The rule which applies to all such reactions as those now under consideration, is that the basicity of the product equals the sum of the basicities of the reagents, minus as many units of basicity as there are atoms of water eliminated.

$$\text{III}^{\circ}.\quad 2H_2SO_4 + A - 2H_2O = Z.$$

In accordance with this reaction, disulphomethylic or methionic acid, disulphethylic or ethionic acid, and the disulphanilic, disulphobenzidic, and disulphonaphthalic acids, have been obtained. Agreeably to the above rule all these products have the properties of bibasic acids. In the actual reactions, Nordhausen acid, or even sulphuric anhydride, is frequently employed.

There are two, if not more, well-defined hydrates of sulphuric acid, namely, the prothydrate $H_2SO_4 . H_2O$, and the deuthydrate $H_2SO_4 . 2H_2O$. The first compound has a specific gravity 1·78, and

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solidifies at 8° or 9°, forming a mass of colourless six-sided prisms, whence it is called glacial sulphuric acid. It boils at 205°—10°, giving off a weak acid vapour. It may be obtained by evaporating any dilute acid at a temperature of 205°, until it ceases to lose water. The second hydrate results from the mixture of one atom of oil of vitriol with two atoms of water. This proportion corresponds with the maximum condensation, nearly 8 per cent., which results from the union of the acid and water. Its specific gravity is 1·62. It boils at 193°, giving off nothing but water until the temperature rises to 205°. It may be obtained by evaporating any more dilute acid at 100°, until it ceases to lose water. Both these hydrates dissolve snow, with production of intense cold.

Sulphuric acid is the starting-point of nearly all important chemical manufactures. Acetic, nitric, and chlorhydric acids are made by its means, and consequently chlorine and bleaching compounds generally. The first stage in the manufacture of commercial soda, or carbonate of sodium, consists in the conversion of chloride of sodium into sulphate of sodium, by the action of sulphuric acid. Saxony blue, so important as a dyestuff, is made by dissolving indigo in sulphuric acid. Super-phosphate of lime, and artificial manures generally, of which many thousand tons are annually consumed in this country, are made by the action of sulphuric acid on bones, coprolites, animal matter, &c. Sulphate of ammonia, sal-ammoniac, ether, phosphorus, corrosive sublimate, and most metallic sulphates, such as Epsom salts or sulphate of magnesium, Glauber's salts or sulphate of sodium, white vitriol or sulphate of zinc, blue vitriol or sulphate of copper, and sometimes green vitriol or sulphate of iron, are produced by its agency. It is also used largely for dissolving silver alloy.

(164) SULPHATES. *Sym.* $HMSO_4$ *acid salt;* M_2SO_4 *normal salt;* $MXSO_4$ *double salt.*—The sulphates constitute a very extensive and important class of salts. *a.* A list of the principal crystalline sulphates, derived from the single atom of sulphuric acid, which are chiefly sulphates of protequivalent metal, is given below. It is observable that the number of atoms of water of crystallisation in different crystallised sulphates is very variable, and that the same sulphate frequently crystallises with two or more different atomic proportions of water. As a rule, the most highly hydrated sulphate of any particular metal is deposited from its solution at the lowest temperature.

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K_2SO_4	Sal polychrest.
Na_2SO_4	Thenardite.
$(NH_4)_2SO_4$	
Ca_2SO_4	Anhydrite.
Sr_2SO_4	Celestine.
Ba_2SO_4	Heavy spar.
$„Cu_4SO_4$	
$„Hg_4SO_4$	
Hg_2SO_4	
Pb_2SO_4	Anglesite.
Ag_2SO_4	
$Sn''SO_4$	
$KHSO_4$	Sal enixum.
$NaHSO_4$	
NH_4HSO_4	
$NaCaSO_4$	Glauberite.
$Li_2SO_4 . H_2O$	
$(NH_4)_2SO_4 . H_2O$	
$Cd_2SO_4 . H_2O$	(Kuhn)
$KCaSO_4 . H_2O$	
$Ca_2SO_4 . 2H_2O$	Selenite.
$Di_2SO_4 . 2H_2O$	
$Fe_2SO_4 . 2H_2O$	
$U_2SO_4 . 2H_2O$	
$Ce_2SO_4 . 3H_2O$	
$2Ce_2SO_4 . 3H_2O$	
$La_2SO_4 . 3H_2O$	
$Di_2SO_4 . 3H_2O?$	
$Cd_2SO_4 . 3H_2O?$	
$KGlSO_4 . 3H_2O$	

$Gl_2SO_4 . 4H_2O$	
$Cd_2SO_4 . 4H_2O$	
$Fe_2SO_4 . 4H_2O$	(Mitscherlich.)
$Mn_2SO_4 . 4H_2O$	
$U_2SO_4 . 4H_2O$	
$NaNH_4SO_4 . 4H_2O$	
$NaZnSO_4 . 4H_2O$	
$Mn_2SO_4 . 5H_2O$	
$Cu_2SO_4 . 5H_2O$	Blue vitriol.
$Zn_2SO_4 . 6H_2O$	(Mitscherlich.)
$Co_2SO_4 . 6H_2O$	
$Ni_2SO_4 . 6H_2O$	
$LiNaSO_4 . 6H_2O$	
$NaMgSO_4 . 6H_2O$	
$KMgSO_4 . 6H_2O$	
$NH_4MgSO_4 . 6H_2O$	
$KZnSO_4 . 6H_2O$	
$KCdSO_4 . 6H_2O$	
$KCuSO_4 . 6H_2O$	
$Na_2SO_4 . 7H_2O$	
$Mg_2SO_4 . 7H_2O$	Epsom salts.
$Zn_2SO_4 . 7H_2O$	White vitriol.
$Mn_2SO_4 . 7H_2O$	
$Cr_2SO_4 . 7H_2O$	
$Fe_2SO_4 . 7H_2O$	Green vitriol.
$Co_2SO_4 . 7H_2O$	
$Ni_2SO_4 . 7H_2O$	
$Na_2SO_4 . 10H_2O$	Glauber's salts.
$Mg_2SO_4 . 12H_2O$	

The sulphates of alkali-metal form hexahydrated double salts, not only with the metals specified in the table, but also with chrome, iron, manganese, nickel, and cobalt. The members of the following sub-groups are known to be isomorphous with one another respectively:—The anhydrous sulphates of potassium and ammonium; the anhydrous sulphates of sodium and silver; the anhydrous sulphates of calcium, strontium, barium, and lead; the pentahydrated sulphates of manganese and copper; the hexahydrated sulphates of zinc, nickel, and cobalt; the hexahydrated double sulphates of potassium, sodium, or ammonium, with magnesium, zinc, cadmium, iron, manganese, chrome, cobalt, nickel, or copper; and the heptahydrated sulphates of magnesium, zinc, iron, manganese, chrome, cobalt, and nickel. Moreover, the magnesian double sulphates with six atoms of

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water, are isomorphous with the magnesian simple sulphates having seven atoms. The simple sulphates of the ferro-magnesian family, which crystallise with five or seven atoms of water, retain one atom with very considerable force. Thus, sulphate of magnesium $Mg_2SO_4 . 7H_2O$, loses six atoms of water at a temperature not greatly exceeding 100°; but it holds back the seventh atom even when heated to upwards of 200°. This last atom of water, retained by the ferro-magnesian sulphates, was termed by Graham constitutional water. Its retention seems to manifest a latent tendency of the sulphates to form quadribasic salts. These monohydrated salts are apparently derived from glacial sulphuric acid $H_2SO_4 . H_2O$.

The protosulphates are for the most part readily soluble in water, but the sulphate of strontium is very nearly, while those of barium and lead are quite insoluble. Moreover, the sulphates of silver, calcium, and, to a less marked extent, potassium, are but sparingly soluble. The protosulphate of mercury does not dissolve in water, but is decomposed thereby into a soluble acid salt, and an insoluble basic salt. Solutions of the protosulphates of lithium, sodium, potassium, ammonium, calcium, magnesium, manganese, and silver are neutral, but those of other normal protosulphates have a marked acid reaction. The anhydrous sulphates of lithium, sodium, potassium, calcium, strontium, barium, and lead are unaffected by a red heat. The other protosulphates are decomposed to a greater or less extent, leaving a residue consisting of, or containing, metallic oxide, save in the case of the sulphates of silver and mercury, which yield reguline metal. The sulphates of magnesium and zinc require a very intense heat to effect their decomposition. Dilute solutions of the sulphates of the highly basylous metals, particularly solutions of gypsum, are slowly decomposed by organic matter, the sulphate being reduced to the state of sulphide or sulphydrate. All sulphates are decomposed by ignition with charcoal; those of lithium, sodium, potassium, calcium, strontium, barium, and lead being reduced to the state of sulphides, those of silver and mercury to the reguline state, and the remainder to the state of oxides or oxisulphides. The majority of normal protosulphates are unaffected by chlorhydric or nitric acid, but the sulphates of alkali-metal and ammonium are converted into acid salts by the exchange of an atom of metal for one of hydrogen. Chlorhydric acid converts the sulphates of silver and lead into their respective chlorides, the latter conversion requiring the assistance of a boiling temperature. At a red heat, the phosphoric, silicic, and boric anhydrides decompose all sulphates more or less

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completely, with evolution of sulphuric anhydride, or more frequently of sulphurous anhydride and oxygen.

The basic sulphates of protequivalent metal are very numerous. They may be looked upon as normal sulphates, together with metallic oxide, replacing the water of hydration of sulphuric acid or of its salts. Thus, we have dibasic sulphate of zinc $Zn_2SO_4 . Zn_2O$, corresponding to glacial sulphuric acid $H_2SO_4 . H_2O$; tribasic sulphate of mercury $Hg_2SO_4 . 2Hg_2O$, corresponding to the second hydrate of sulphuric acid $H_2SO_4 . 2H_2O$; and tribasic sulphate of copper $Cu_2SO_4 . 2Cu_2O . 3H_2O$, corresponding to blue vitriol $Cu_2SO_4 . 5H_2O$. Much more highly basic sulphates of metal may be obtained. The majority of basic protosulphates are insoluble in water. Those few which are soluble are decomposed by a great excess of water into metallic oxide or hydrate, and normal sulphate of metal.

β. The most important sulphates derived from the double atom of sulphuric acid $H_4(SO_4)_2$, are the double sulphates of sesqui-equivalent metals, and particularly those known as the alums. It obviously requires more than one atom of a bihydric acid to contain the hydrogen replaceable by a ter-equivalent radicle. Hence, in the formation of the alums and pseudo-alums, two atoms of sulphuric acid, containing four atoms of hydrogen, take part. Three of these hydrogen-atoms are replaced by a double atom of metal having a terequivalent function, while the fourth is replaced by a protequivalent atom, usually of a highly basylous metal. Thus, common potassium alum is represented by the formula $(Al_2)'''K(SO_4)_2$, or $All'''K(SO_4)_2$, and is derived from two atoms of sulphuric acid $H_4(SO_4)_2$. This salt crystallises with twelve atoms of water, in the form of regular octahedrons, sometimes simple, but usually more or less modified. The sodium and ammonium alums correspond in constitution to, and are isomorphous with potassium alum. Thus we have:—

$$Al_2K(SO_4)_2 . 12H_2O$$
$$Al_2Na(SO_4)_2 . 12H_2O$$
$$Al_2(NH_4)(SO_4)_2 . 12H_2O$$

Now in any one of these alums, the double atom of aluminum may be replaced by a double atom of chromium Cr_2''' or Ccr''', or of iron Fe_2''' or Ffe''', or of manganese Mn_2''' or Mm''', without affecting either the water of crystallisation, or the form of the resulting salt. These octahedral double sulphates of sesqui-equivalent and protequivalent metals, having twelve atoms of water, constitute the genuine alums. The existence of sodium-iron and sodium-

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manganese alum is doubtful, but the potassium- and ammonium-iron and manganese alums are well known. In addition to the above-described alums, we are acquainted with several pseudo-alums which are derived in the same manner from two atoms of sulphuric acid, but which have a different number of atoms of crystallisation-water, or a different crystalline form from the genuine alums. Thus we have:—

$$Mn_2K(SO_4)_2$$
$$Fe_2Fe(SO_4)_2$$
$$Cr_2K(SO_4)_2 \,.\, 6H_2O$$
$$Al_2Mn(SO_4)_2 \,.\, 12H_2O$$
$$Al_2Fe(SO_4)_2 \,.\, 12H_2O, \text{ \&c.}$$

The genuine alums are all soluble in water, forming solutions which have a styptic taste and marked acid reaction. The first effect of heat upon the alums is to drive off their water of crystallisation; a further degree of heat renders the dried residues very difficultly soluble in water; while a still higher temperature converts them into basic salts by the loss of sulphuric anhydride. The ammonium alums, when very strongly heated, leave a residue of pure sesquioxide. The fixed-alkali alums leave a residue of sesquioxide, mixed with sulphate of alkali metal. It requires a very powerful and prolonged heat to drive off the last traces of sulphuric acid from the sesqui-oxides thus produced.

Most of the alums yield more or less defined basic salts. The best known of these is the native crystalline alum-stone having the formula $Al_2K(SO_4)_2 \,.\, Al_4O_3 \,.\, 4H_2O$. It corresponds in composition with the basic ammonium alum formed by digesting gelatinous alumina in a hot solution of the normal alum, and having the formula $Al_2NH_4(SO_4)_2 \,.\, Al_4O_3 \,.\, 4H_2O$.

γ. The simple sulphates of the sesqui-equivalent and terequivalent metals are derived from the treble atom of sulphuric acid $H_6(SO_4)_3$. These salts owe the comparative complexity of their constitution to the circumstance of the terequivalency of the single or double atom of metal adapting itself badly to the bihydric character of the acid. Thus, for instance, Bi''' represents the smallest combining proportion of bismuth, which proportion, however, is equivalent to three atoms of hydrogen. Hence one and a half atoms of sulphuric acid are required to furnish the hydrogen replaceable by one, or three atoms of acid to furnish the hydrogen replaceable by two atoms of bismuth; so that the molecule of normal sulphate of bismuth consists of two atoms of bismuth and three atoms of the sulphuric residue SO_4, thus: $Bi_2'''(SO_4)_3$.

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Similarly, the double atom of aluminum constitutes its smallest combining proportion, and replaces three atoms of hydrogen; whence twice this proportion is required to replace the six atoms of hydrogen furnished by the treble atom of sulphuric acid. The following list comprises the principal normal ter- and sesquisulphates: —

	$Bi_2(SO_4)_3$
	$Sb_2(SO_4)_3$
	$Mn_4(SO_4)_3$
	$Cr_4(SO_4)_3$
Coquimbite	$Fe_4(SO_4)_3 \cdot 9H_2O$
	$Cr_4(SO_4)_3 \cdot 15H_2O$
Hair-salts	$Al_4(SO_4)_3 \cdot 18H_2O$

These salts dissolve in water, forming strongly acid solutions. They are decomposed by heat into sulphuric anhydride and metallic oxide. A very large number of insoluble basic sulphates of sesqui-equivalent metal are also known, as illustrated by the following list of some of the best defined basic sulphates of ferricum: —

Fibrous coquimbite	$2\{Fe_4(SO_4)_3\}\ Fe_4O_3 \cdot xH_2O$
Fibro-ferrite . .	$Fe_4(SO_4)_3 \cdot Fe_4O_3 \cdot 18H_2O$
Tribasic sulphate .	$Fe_4(SO_4)_3 \cdot 2Fe_4O_3 \cdot 3H_2O$
Vitriol ochre . .	$Fe_4(SO_4)_3 \cdot 5Fe_4O_3 \cdot 6H_2O$
Ennabasic sulphate	$Fe_4(SO_4)_3 \cdot 8Fe_4O_3 \cdot 12H_2O$

The two principal basic sulphates of aluminum have the respective formulæ, $Al_4(SO_4)_3 \cdot Al_4O_3 \cdot xH_2O$, corresponding to that of fibro-ferrite, and $Al_4(SO_4)_3 \cdot 2Al_4O_3 \cdot 9H_2O$, which represents the composition of the mineral aluminite.

The so-called basic sesquisulphate of uranium appears to be in reality a protosulphate of uranyl $(U_2O)_2SO_4$, derived from a single molecule of sulphuric acid by the substitution of two atoms of the oxidised protequivalent radicle uranyl for the two atoms of hydrogen. It crystallises in the form of yellow needles, is freely soluble in water, and combines with sulphate of potassium to form a crystalline double salt $K(U_2O)SO_4 \cdot H_2O$. Similar soluble sulphates of ferryl and aluminyl have been described, but they are very unstable; the solution of sulphate of ferryl, for instance, being readily converted into the insoluble basic sulphate of ferricum, thus: —

$$3\{(Fe_2O)_2SO_4\} + 3H_2O = Fe_4(SO_4)_3 \cdot 2Fe_4O_3 \cdot 3H_2O.$$

(165) Many sulphates occur native in a crystalline or semi-crystalline condition. The principal of these are aphthalose K_2SO_4; thenardite Na_2SO_4; anhydrite and selenite, Ca_2SO_4 and Ca_2SO_4.

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$2H_2O$, respectively; celestine Sr_2SO_4; heavy spar Ba_2SO_4; glauberite $NaCaSO_4$; anglesite Pb_2SO_4; coquimbite $Fe_4(SO_4)_3 . 9H_2O$; and hair-salts $Al_4(SO_4)_3 . 18H_2O$. Sulphate of magnesium exists to a considerable extent in sea-water, from which it is sometimes procured by evaporation and crystallisation; while most natural waters contain greater or less quantities of the sulphates of magnesium, calcium, and sodium. The sulphates are procured by very many processes:—

a. The sulphates of zinc and iron are frequently prepared by the action of dilute sulphuric acid upon the respective metals, as in the ordinary methods of making hydrogen gas. The sulphates of copper, mercury, and silver are obtained by acting upon the respective metals with a stronger acid, and at an increased temperature, whereby sulphurous acid is evolved. The sulphuric acid used for dissolving silver is frequently mixed with nitric acid, in which case nitric oxide gas, instead of sulphurous acid, is evolved.

β. Many sulphates are formed by the action of sulphuric acid upon metallic oxides, hydrates, or salts. Thus the sulphates of magnesium and aluminum are made commercially by dissolving crude magnesia and alumina, respectively, in sulphuric acid. Other sulphates result from the processes used for the liberation of various acids, usually volatile acids, by treating the salts of these acids with sulphuric acid. Sulphate of sodium, for instance, is a residue from the processes of making chlorhydric, nitric, and acetic acids, by acting with sulphuric acid upon the chloride, nitrate, and acetate of sodium, respectively. In a somewhat similar manner, sulphate of calcium is a residue of the processes for making phosphoric, tartaric, and citric acids, by treating with sulphuric acid the phosphate, tartrate, and citrate of lime, respectively. Sulphate of ammonium is procured on a very large scale by neutralising with sulphuric acid the ammoniacal liquor of gas works, which consists principally of a solution of carbonate and sulphydrate of ammonium.

γ. Some sulphates are made by the oxidation of sulphides. In this way the sulphates of zinc, iron, and copper are sometimes produced, by gently roasting their respective sulphides and lixiviating. Sulphide of iron, moreover, is convertible into the sulphate, by the simple process of weathering or exposing to air. Sulphate of aluminum also, in the form of plumose alum, is a secondary result of the weathering of pyritic shales.

δ. Many sulphates are obtained by the decomposition of other sulphates. Thus, sulphate of copper is made by the action of

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metallic copper upon the sulphate of silver produced in the process of refining. Similarly, sulphate of iron results from the action of scrap iron upon solutions of sulphate of copper. The constituent sulphate of potassium in common alum is generally formed by the mutual decomposition of chloride of potassium and sulphate of iron. Sulphate of sodium is obtained as a by-product in the manufacture of sal-ammoniac and corrosive sublimate, by distilling with common salt the sulphates of ammonium and mercury, respectively. It also results from the fusion of the insoluble sulphates of barium, strontium, calcium, and lead with carbonate of sodium.

The above insoluble sulphates of metal are formed by the addition of sulphuric acid, or a soluble sulphate, to a soluble salt of any one of the respective metals. A solution containing sulphuric acid, or any soluble sulphate, gives, with a solution of chloride or nitrate of barium, a white precipitate of sulphate of barium, insoluble in chlorhydric acid, and in dilute nitric acid. When this precipitate, or any other sulphate, is mixed with carbonate of sodium and charcoal, and heated in the reducing flame of the blow-pipe, a fused mass is obtained, which, when moistened with water, produces a brown stain upon silver foil, and, when treated with dilute chlorhydric acid, evolves sulphydric acid gas, recognisable by its action upon lead paper.

Thiosulphuric Acid and Salts (Hyposulphites).

(166) Thiosulphuric Acid. *Sym.* $H_2S_2O_3$; *p. n.* 114.—This acid is scarcely known in the free state. No sooner is it produced by the action of a stronger acid upon any of its salts, than it is decomposed into sulphurous acid and sulphur, which is deposited in the plastic condition. According to Herschell, the acid is not decomposed immediately, and according to Rose, a very small quantity may remain unaltered for several weeks.

(167) Thiosulphates, or Hyposulphites. *Sym.* $M_2S_2O_3$.—These salts are procurable by several processes, of which the principal are:— *a.* By passing sulphurous acid through a solution of alkaline sulphide; or, better, by digesting, or boiling, sulphur with a solution of alkaline sulphite: $Na_2SO_3 + S = Na_2S_2O_3$.

β. By boiling sulphur with a solution of alkaline hydrate, we obtain thiosulphate and pentasulphide of alkali, thus: $6CaHO + S_{12} = Ca_2S_2O_3 + 2Ca_2S_5 + 3H_2O$. By exposing this solution to the air until it becomes colourless, the pentasulphide is decomposed into sulphur and thiosulphate, $Ca_2S_5 + O_3 = Ca_2S_2O_3 + S_3$.

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γ. When certain metals, notably zinc and iron, are dissolved in aqueous sulphurous acid, we have mixtures of sulphite and thiosulphate produced, thus: $Zn_4 + 3H_2SO_3 = Zn_2SO_3 + Zn_2S_2O_3 + 3H_2O$.

The alkaline thiosulphates, and those of magnesium and zinc, are soluble in water. That of barium, however, is only sparingly soluble, and may be obtained as a crystalline precipitate by mixing solutions of chloride of barium and thiosulphate of sodium. Solutions of the thiosulphates of calcium and strontium are decomposed by ebullition with separation of sulphur. The thiosulphate of sodium is a comparatively permanent salt, which crystallises in fine rhombic prisms. When heated, it breaks up into sulphate and pentasulphide of sodium. According to Kane, the thiosulphate, and another salt which may be termed the dithiosulphate of sodium, are isomorphous with ordinary sulphate of sodium, and, like it, possess each a point of maximum solubility in water below the boiling points of their respective solutions.

Sulphate	$Na_2S\ O_4 . 10H_2O$
Thiosulphate . . .	$Na_2S_2O_3 . 10H_2O$
Dithiosulphate . .	$Na_2S_3O_3 . 10H_2O$

With the salts of most heavy metals, the soluble thiosulphates give precipitates which, especially on the addition of an acid, or by an increase of temperature, are converted wholly or partly into sulphide. The reaction with a metallic oxide is very simple, and moreover, exhibits the relation of the thiosulphates to the normal or oxysulphates, thus: $Hg_2O + Na_2S_2O_3 = Hg_2S + Na_2SO_4$. The alkaline thiosulphates dissolve the halogen salts of silver, forming double salts of a remarkably sweet taste, thus: $AgCl + Na_2S_2O_3 = NaCl + AgNaS_2O_3$. The thiosulphates, or hyposulphites, are much used for fixing photographic pictures, the thiosulphate of sodium being usually selected for the purpose. The photographic paper, or glass, uniformly coated with some silver compound, is exposed in the camera or press, and then immersed in a solution of the thiosulphate, which dissolves the silver away from those parts of the picture which have not been acted upon by light, and converts the silver compound that has been acted upon into unalterable sulphide of silver. A crystalline double thiosulphate of sodium and gold $AuNa_3(S_2O_3)_2 . 2H_2O$, was prepared by Fordis and Gelis, by mixing concentrated solutions of terchloride of gold and thiosulphate of sodium, precipitating with alcohol, dissolving in water, and reprecipitating with alcohol. This salt is used both in daguerreotype and ordinary photographic processes. The soluble

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thiosulphates decolorise tincture of iodine, with formation of tetrathionates. Thiosulphate of sodium has almost superseded acid-sulphite of sodium as an *antichlore*, or agent for removing the last traces of chlorine, or hypochlorous acid, from substances which have been bleached therewith.

POLYTHIONIC ACIDS AND SALTS.

ACIDS.		SALTS.
Dithionic . . .	$H_2S_2O_6$	$Mn_2S_2O_6$ Dithionate of manganese.
Trithionic . . .	$H_2S_3O_6$	$K_2S_3O_6$ Trithionate of potassium.
Tetrathionic . .	$H_2S_4O_6$	$Ba_2S_4O_6$ Tetrathionate of barium.
Pentathionic . .	$H_2S_5O_6$	$Ba_2S_5O_6$ Pentathionate of barium.

(168) These acids and salts have many properties in common with one another, and are all more or less unstable. The acids are decomposed by boiling, the dithionic into sulphuric acid and sulphurous anhydride, the other three into sulphuric acid, sulphurous anhydride, and sulphur. According to Kessler, the pentathionic acid yields at first sulphuretted hydrogen, and the tetrathionic is not decomposed by boiling, save in the presence of chlorhydric acid, when it also yields a trace of sulphuretted hydrogen. The polythionates when heated, frequently even when boiled, yield sulphate of metal, sulphurous anhydride, and, except in the case of the dithionates, sulphur, thus: $Ba_2S_4O_6 = Ba_2SO_4 + SO_2 + S_2$. The acidified solutions of the salts, unlike those of the thiosulphates, do not evolve sulphurous anhydride or acid until heated, and then, in the case of the dithionates, there is no deposition of sulphur. The acidified solutions of the salts act more or less powerfully as reducing agents. By treatment with boiling nitric acid, the salts are oxidated into sulphate, sulphuric acid, and usually, except as regards the dithionates, sulphur. The trithionates, when gently heated with solution of hydrate of potassium, are decomposed into sulphate and thiosulphate. Under the same circumstances, the tetra- and penta-thionates yield sulphide of potassium in addition. The tri- tetra- and penta-thionates yield, with salts of the heavy metals, precipitates which either spontaneously, or by boiling, become converted, more or less completely, into sulphides.

(169) DITHIONIC OR HYPOSULPHURIC ACID. *Sym.* $H_2S_2O_6$; *p. n.* 162.—When sulphurous anhydride is passed through water in which finely-divided peroxide of manganese is suspended, it is completely absorbed; and, provided the temperature be kept down, dithionate of manganese is formed in solution, thus: $Mn_2O_2 + 2SO_2 = Mn_2S_2O_6$. There is always produced in addition a little sulphate of manganese, which, at increased temperatures, constitutes almost the sole product.

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By adding hydrate of barium to the impure dithionate of manganese, we have hydrate of manganese and sulphate of barium precipitated, and dithionate of barium left in solution. By carefully precipitating the barium therefrom by an exact sufficiency of sulphuric acid, we obtain a solution of dithionic acid, which may be concentrated in vacuo over oil of vitriol until its sp. gr. reaches 1.347. The acid dissolves zinc, with evolution of hydrogen, forming a dithionate. All its salts are soluble in water. They are decomposed by heat into sulphate of metal and sulphurous anhydride, thus:—

$$K_2S_2O_6 = K_2SO_4 + SO_2 \text{ (\textit{vide supra}).}$$

(170) TRITHIONIC ACID. *Sym.* $H_2S_3O_6$; *p. n.* 194.—When a saturated solution of bisulphite of potassium is digested with sulphur for some days, at a moderate temperature, until the yellow colour first produced has disappeared, evolution of sulphurous acid takes place, and there is left in solution trithionate of potassium with some sulphate and thiosulphate. The trithionate, which is only moderately soluble, may be purified by crystallisation. It occurs in four-sided prisms with dihedral summits. When its solution is carefully precipitated with tartaric or perchloric acid, trithionic acid is left in solution, and may be concentrated by evaporation in vacuo over oil of vitriol.

(171) TETRATHIONIC ACID. *Sym.* $H_2S_4O_6$; *p. n.* 226.—When iodine is added to thiosulphate of barium suspended in a small quantity of water, iodide and tetrathionate of barium are formed, thus: $2Ba_2S_2O_3 + I_2 = Ba_2S_4O_6 + 2BaI$. The sparingly soluble tetrathionate partially crystallises out, and may be completely separated by means of strong alcohol, which removes the iodide of barium and free iodine. The salt may then be dissolved in water, and crystallised by spontaneous evaporation of the solution. The acid may be prepared by precipitating the barium of the salt with an exact sufficiency of sulphuric acid, and concentrating the filtrate in vacuo over oil of vitriol. Tetrathionic acid is moderately stable.

(172) PENTATHIONIC ACID. *Sym.* $H_2S_5O_6$; *p. n.* 258.—This acid may be produced by the action of aqueous sulphurous acid upon protosulphide of chlorine; or, as we have already seen, by the mutual decomposition of sulphurous and sulphydric acids:—

$$5H_2SO_3 + 5H_2S = H_2S_5O_6 + 9H_2O + S_5.$$

Sulphurous and sulphydric gases are alternately passed through water, until a considerable deposit of sulphur has taken place. A little carbonate of barium is added to the filtrate to re-

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move sulphuric acid, and the liquid, after refiltration, concentrated, first in a water bath, then in vacuo over oil of vitriol. The pentathionates are very unstable, having a strong tendency to decompose into tetrathionates and sulphur. The barium salt may be obtained in well-defined crystals, by neutralising the acid with hydrate of barium, and precipitating with strong alcohol.

§ III. Selenium.

Symbol, Se; *Proportional number*, 79·5; *Vapour density*, 79·5; *Atomic volume*, □.

(173) Selenium is a substance closely allied in its properties to sulphur. Though a very sparingly distributed element, it enters into the composition of many minerals. Riolite consists of free selenium, mixed with seleniferous sulphur and metallic selenides. In the sulphur from the Lipari Islands, selenium also presents itself as an impurity. It is found to a greater or less extent in the iron pyrites of certain localities, particularly Fahlun in Sweden, and Kraslitz and Luckawitz in Bohemia; also in some forms of copper pyrites, those from Rammelsberg and Anglesea, for instance. It occasionally occurs in small quantities associated with other sulphides, as those of lead and molybdenum; also in tellurium ores. Native selenides of cadmium, iron, cobalt, nickel, copper, mercury, lead, and silver are known to mineralogists. The principal sources of selenium are the double selenide of lead and copper, and the deposit which occurs in the leaden chambers of vitriol factories, where seleniferous sulphur, usually pyritic, is employed. It was in this last substance, derived from Fahlun pyrites, that Berzelius originally discovered selenium, in 1817. It takes its name from *σελήνη*, the moon.

(174) *α.* Selenium is thus obtained from the cuproplumbic selenides of the Harz. The ore is pulverised, and treated with chlorhydric acid to dissolve the earthy carbonates. The washed and dried residue is mixed with an equal weight of black flux and ignited for some time. By this means, the selenium is converted into selenide of potassium, which, by treatment with boiling water, is dissolved away from the resulting oxides. By exposure to air, this solution absorbs oxygen, and liberates its selenium as a grey deposit, which is washed, dried, and distilled.

β. The seleniferous deposit from certain vitriol works, as those

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near Fahlun, is mixed with nitrate and carbonate of potassium, and deflagrated in a red-hot crucible. The residue, containing seleniate of potassium, is treated with dilute chlorhydric acid, and the whole evaporated down to a small bulk, whereby a reducing action is exerted, and selenious acid set free. The liquid is then saturated with sulphurous acid, and heated to the boiling point, when the selenium is deposited in red amorphous flakes.

(175) Selenium, like sulphur, occurs in different allotropic conditions. The soluble modification includes several varieties. Crystalline selenium is produced by the slow action of air upon solutions of the selenides and selenhydrates. It is deposited from the solution of selenium in bisulphide of carbon, by the spontaneous evaporation of the solvent. It is also deposited on cooling a saturated solution of selenium in oil of vitriol. It may sometimes be obtained by the very slow cooling of melted selenium. It, moreover, results from the spontaneous conversion of vitreous selenium, and especially by heating vitreous selenium to a temperature of 125° and upwards. Crystalline selenium occurs in four-sided prisms, of which the system of crystallisation is not well ascertained. It is not improbably dimorphous. Its sp. gr. is 4·5 — 8. It melts at 211·5° without previous softening. It is slightly soluble in bisulphide of carbon, and conducts electricity, its conducting power increasing rapidly with its temperature. The amorphous selenium precipitated by exposing solution of selenhydric acid to air, and that produced by the electrolysis of selenhydric acid are also soluble in bisulphide of carbon.

Vitreous selenium results from the solidification of the element after fusion. It occurs as a brittle solid having a glassy fracture, almost metallic lustre, and deep brown colour. Its sp. gr. is 4·3. It is scarcely at all soluble in bisulphide of carbon, does not conduct electricity, but becomes slightly electrical by friction in a dry atmosphere. At ordinary temperatures it very slowly changes into the crystalline variety, acquiring a dull grey colour and fine-grained fracture. By trituration, vitreous selenium yields a dark red powder, and is changed into the crystalline modification. By the action of heat, the transformation of vitreous selenium is effected very readily, particularly at a temperature of 125-30°, when the mass becomes suddenly crystalline, the temperature rising spontaneously to above 200°. Vitreous selenium softens almost to melting in boiling water, remains in a plastic condition for some time, and may be drawn into threads like sealing-wax. The most insoluble or electro-positive selenium results from the electrolysis of selenious acid, whereby the selenium is deposited at the negative

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pole, and from the reduction of selenious acid by sulphurous acid. Like vitreous selenium, this last variety manifests a great rise of temperature when heated.

Selenium is quite insoluble in water, cold or hot. It is soluble to some extent in oil of vitriol, but is precipitated by dilution. It is not readily combustible, though, when thoroughly heated, it burns with a blue flame; but, at the same time, it evolves yellowish-red vapours of unoxidised selenium, and probably also of a protoxide of selenium, to which last compound the peculiar odour of burning selenium is usually attributed. Selenium, heated in close vessels, boils below a red heat, and is converted into a deep yellow vapour, which condenses in scarlet flowers or dark lustrous drops, according to the size of the condenser. At temperatures not greatly exceeding the boiling-point of selenium, the density of its vapour, like that of sulphur vapour under similar circumstances, is anomalous; but at upwards of 1000° it is 79·5 times that of hydrogen at the same temperature.

Selenhydric Acid.

Symbol, H_2Se; *Proportional number,* 81·5; *Density,* 40·75; *Atomic volume,* □□.

(176) This gas, also known as selenetted hydrogen, is obtained by the action of dilute chlorhydric or sulphuric acid upon the selenides of potassium, iron, &c. precisely as sulphydric acid is obtained from the sulphides: $Fe_2Se + H_2SO_4 = H_2Se + Fe_2SO_4$. Selenhydric acid is a colourless, inflammable gas. It is soluble in water, and cannot long be preserved over mercury. It has a most offensive acrid odour, impairing, or even destroying, the sense of smell for several hours. Its aqueous solution absorbs oxygen from the air, and deposits selenium. This solution also, like that of sulphydric acid, has a hepatic taste, a slight acid reaction, and gives precipitates in the solutions of the majority of the metals, those of manganese, zinc, and cerium being flesh-coloured, the remainder being brown or black.

Selenides and Selenhydrates.

(177) These compounds correspond closely, in their formulæ, properties, and modes of formation, to the sulphides and sulphydrates. We have the usual varieties, proto-, bi-, ter-, &c. selenides. The selenides of alkali-metal result from heating their respective

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carbonates with charcoal and selenium or selenious anhydride. The selenhydrates are obtained by passing selenhydric acid gas into solutions of caustic alkali. The alkaline selenides and selenhydrates are soluble in water, forming solutions which are decomposed by exposure to air, with deposition of selenium. The usual reddish tint of these solutions is probably due to the presence of some free selenium dissolved therein. The majority of the selenides are formed by fusing together the metal and selenium. Several of them occur native, as rare minerals, or as impurities in the sulphides. The insoluble selenides may also be obtained by decomposing solutions of metallic salts with selenhydric acid or an alkaline selenhydrate.

(178) CHLORIDES OF SELENIUM.—We have no chloride of selenium analogous to the protochloride of sulphur Cl_2S, or to selenhydric acid H_2Se, in which the hydrogen is replaced by chlorine. But we have a dichloride of selenium, or perselenide of chlorine Cl_2Se_2, analogous to the persulphide of chlorine Cl_2S_2, and to the persulphide of hydrogen H_2S_2. It is a brownish, oily, volatile substance, heavier than water, and slowly decomposed thereby. It results from the action of chlorine upon selenium. There is also a quadrichloride of selenium $SeCl_4$, which results from the action of an excess of chlorine upon selenium. It is a volatile, white crystalline mass, immediately decomposed by water into chlorhydric and selenious acids:—

$$SeCl_4 + 3H_2O = 4HCl + H_2O.SeO_2, \text{ or } H_2SeO_3.$$

Selenious chloraldehyd Cl_2SeO, has been obtained by Weber as a heavy yellowish fuming liquid. Selenic chloraldehyd Cl_2SeO_2, has not been described.

(179) OXIDE OF SELENIUM.—A substance the nature of which is not satisfactorily demonstrated. It results from the imperfect combustion of selenium in air or oxygen, and is the source of the peculiar horse-radish smell evolved in such experiments. It is a colourless gas, sparingly soluble in water, and having no acid reaction.

SELENIOUS ANHYDRIDE, ACID, AND SALTS.

(180) SELENIOUS ANHYDRIDE. *Sym.* SeO_2; *p.n.* 111·5.—This compound may be obtained by burning selenium in a current of oxygen gas; or by evaporating the solution of the acid to dryness, in which last case it presents itself as a white mass which does not melt, but which, at a heat somewhat below redness, sublimes in the

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form of a yellow vapour, condensing in white four-sided needles. It absorbs water rapidly, reproducing the acid.

(181) SELENIOUS ACID. *Sym.* H_2SeO_3; *p. n.* 129·5.—This acid results from the hydration of the anhydride, or from the action of boiling nitric or nitromuriatic acid upon selenium. From its hot aqueous solution, it is deposited on slow cooling in prismatic nitre-like crystals. By heat, it breaks up into water and the anhydride, which a much greater heat sublimes. Its solution has an acid burning taste, and is reduced, especially at a boiling heat, by sulphurous acid, or a sulphite, with deposition of selenium. All the metals also, with the exception of gold, palladium, and platinum, effect its decomposition with separation of selenium. Sulphydric acid reacts upon its solution to form a sulphide of selenium, thus:—

$$H_2SeO^3 + 2H_2S = 3H_2O + SeS_2.$$

Selenious acid has the well-defined characters of a powerful acid. It reddens litmus paper, neutralises alkalies, effervesces with carbonates, forms neutral and acid salts, and precipitates the neutral soluble salts of lead and silver.

(182) SELENITES. — The normal salts, like the sulphites, are either neutral or acid, M_2SeO_3 or $HMSeO_3$. The acid selenites of the alkalies seem also to form double salts with an additional atom of selenious acid, thus: $HKSeO_3 . H_2SeO_3$. The neutral selenites have a purely saline taste. They are decomposed when heated with charcoal, forming selenides, or metallic oxide and selenium. When heated with carbonate of sodium in the inner blow-pipe flame, they emit the characteristic horse-radish odour. The fused mass, moistened with water, produces a brown stain on silver foil. The selenites, save those of the alkalies, are insoluble in water, but soluble in nitric acid, those of lead and silver, however, only with difficulty. Solutions of selenites in chlorhydric acid are decomposed by sulphurous acid, with deposition of selenium, in the form of a reddish-brown precipitate.

SELENIC ACID AND SALTS.

(183) SELENIC ACID. *Sym.* H_2SeO_4; *p. n.* 145·5.—*a.* This acid may be obtained by treating selenious acid, or finely-divided selenium suspended in water, with chlorine gas. Selenium boiled in nitric acid yields only selenious acid. *β.* It is usually made by decomposing, with sulphydric acid, the seleniate of lead suspended in water: $Pb_2SeO_4 + H_2S = H_2SeO_4 + Pb_2S$. The filtrate is to be evaporated down until its sp. gr. reaches 2·6. The product is not

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pure selenic acid, but always contains a little water in addition, which cannot be driven off without decomposing the acid. Selenic acid is a liquid resembling sulphuric acid in many of its properties. It is very hygroscopic, and its mixture with water is attended by a considerable elevation of temperature. The strong or dilute acid, when boiled with chlorhydric acid, liberates chlorine, and is reduced to the state of selenious acid. The strong acid, when heated, breaks up into selenious anhydride, water, and oxygen. Selenic acid, though so easily reducible, differs from selenious acid in withstanding the decomposing action of sulphurous and sulphydric acids. Moreover, its solutions dissolve zinc and iron, with mere substitution of the metal for hydrogen.

(184) SELENIATES. *Sym.* M_2SeO_4.—The alkaline seleniates are usually made by igniting selenium, selenides, or selenites with the nitrates of potassium or sodium, and purifying the resulting seleniate by crystallisation. Other seleniates are made by dissolving metallic oxide, hydrate, or carbonate in selenic acid. The only insoluble seleniates, namely, those of barium, strontium, and lead, may be obtained by precipitating their soluble salts with seleniate of alkali-metal. These seleniates are not dissolved even by nitric acid. The seleniates correspond very closely in their properties to the sulphates, with which they are isomorphous. Most of them sustain a red heat without decomposition. Heated in a current of hydrogen gas, they are readily converted into selenides. Heated with charcoal or with carbonate of sodium, in the reducing flame, they are also reduced to selenides, and give off the characteristic selenium smell. Boiled with chlorhydric acid, they evolve chlorine, and leave selenious acid, from which selenium may be precipitated by sulphurous acid.

(185) SULPHIDES OF SELENIUM.—These correspond to the selenious and selenic anhydrides respectively. The bisulphide SeS_2, results from the action of sulphydric acid upon solution of selenious acid, as we have seen. It occurs as a bright yellow precipitate, which becomes darker by drying. It melts at a little above 100°, and at a higher temperature distils unchanged. The tersulphide SeS_3, is a fusible volatile solid, of a brick-red colour, made by fusing one atom of selenium with three of sulphur. Both sulphides dissolve in solutions of alkaline sulphydrate.

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§ IV. Tellurium.

Symbol, Te; *Proportional number*, 129.

(186) Tellurium is found in a very few localities only, principally in Hungary and Transylvania. It occurs native in a state of considerable purity, and has also been met with in the form of tellurous anhydride. Its principal ores are the telluride of bismuth, and the foliated or graphic tellurium, which contains tellurides of lead, silver, and gold. The separate tellurides of lead and silver also are sometimes met with tolerably pure. Tellurium was first identified as a distinct metal by Klaproth, in 1798, who gave it the name it now bears, from *tellus*, the mythological name of the earth.

(187) Tellurium is prepared by processes analogous to those which yield selenium. *α*. Native telluride of bismuth, freed as far as possible from its matrix, and made into a paste with carbonate of potassium and oil, is gradually heated in a well-covered crucible, to a full white heat. Boiling water extracts telluride of potassium from the fused mass, forming a port-wine-coloured solution, from which the tellurium is deposited in metallic scales by the passage of a current of air through it, or by mere exposure to air. *β*. Finely-pulverised foliated tellurium, freed from the sulphides of lead and antimony by repeated boiling with chlorhydric acid and washing with water, is heated with strong nitric acid, whereby tellurous acid is obtained in solution. This is evaporated to dryness, and the residue, after solution in chlorhydric acid, is reduced by a current of sulphurous anhydride.

(188) Tellurium, though decidedly metallic, is yet a member of the sulphur family. The gradual transition from the non-metallic to the metallic character, in elements belonging to the same natural group, is manifested to an equal, or even greater, extent in the classes presently to be described.

Tellurium is a brilliant, crystalline, brittle metal, somewhat paler than bismuth. It assumes a rhombohedral form, and is isomorphous with antimony and arsenic. It conducts heat and electricity, though imperfectly. Its sp. gr. is 6·25. It melts at a temperature of about 500°. It volatilises at a higher temperature, and may be purified by distillation in a current of hydrogen. It condenses in crystalline needles, or in drops. Like sulphur and selenium, it is dissolved to a slight extent by concentrated oil of vitriol, and may be precipitated therefrom unchanged by dilution. When

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strongly heated in the air, it takes fire, burns with a lively blue flame edged with green, producing white fumes of tellurous acid, and developing a peculiar odour said to be in part due to the presence of traces of selenium.

Tellurhydric Acid.

Symbol, H_2Te; *Proportional number*, 131; *Vapour density*, 65·5; *Atomic volume*, □□.

(189) This gas, also called telluretted hydrogen, is evolved by treating with chlorhydric acid, certain metallic tellurides, usually that of zinc, which is made for the purpose by fusing zinc with tellurium: $Zn_2Te + 2HCl = H_2Te + 2ZnCl$. Tellurhydric acid gas closely resembles sulphydric acid. It has a very similar smell, burns with a blue flame, has a slight acid reaction, precipitates most of the metals from their solutions, and dissolves in water, forming a colourless liquid which, by exposure to air, deposits tellurium.

Tellurides and Tellurhydrates.

(190) The tellurides belong to the class of metallic alloys. Those of bismuth, gold, and silver are found native. The others may be obtained by fusing the respective metals with tellurium. Tellurides M_2Te, may also be obtained in the wet way by precipitating solutions of the metals with tellurhydric acid, or an alkaline tellurhydrate. The tellurides of potassium and sodium are made by heating powdered tellurium with a carbonate of alkali-metal containing finely-divided charcoal, black flux for instance. The access of air to the mass must be prevented until it has become quite cold, on account of its highly pyrophoric nature. It may then be extracted with water, in which these alkaline tellurides dissolve, with probable conversion into tellurhydrates. They may also be formed by passing tellurhydric gas through solutions of alkaline hydrate or ammonia. Tellurhydrate solutions have a port-wine colour, and deposit tellurium by the action of air.

(191) Chlorides of Tellurium.—We have two chlorides of tellurium, namely, a bichloride $TeCl_2$, and a tetrachloride $TeCl_4$. They are both volatile, and decomposible by excess of water, the latter being completely converted into tellurous and chlorhydric acids: $TeCl_4 + 3H_2O = 4HCl + H_2TeO_3$. The tetrachloride unites with the chlorides of alkali-metals to form crystalline double salts. The bromides and iodides of tellurium correspond to the chlorides in their properties and composition.

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Tellurous Anhydride, Acid, and Salts.

(192) **Tellurous Anhydride.** *Sym.* TeO_2; *p. n.* 145.—This compound may be prepared by a low ignition of the precipitated acid. Moreover, the aqueous solution of the acid, when gently heated, is decomposed into water and anhydride, which last is deposited in semi-crystalline grains. The same change takes place spontaneously, though more rapidly on the application of heat, in the nitric acid solution of tellurous acid. In this case, the deposit of anhydride is much more abundant, and, if slowly produced, is distinctly crystalline, showing here and there well-defined octahedrons. The anhydride, though soluble to a slight extent in water, has no action upon litmus. It is fusible and volatile. The fused anhydride is a clear transparent deep yellow liquid, which congeals into a white highly crystalline mass. When fused with alkaline hydrates or carbonates, it forms tellurites.

(193) **Tellurous Acid.** *Sym.* H_2TeO_3; *p. n.* 163.—*a.* This acid is best obtained by decomposing tetrachloride of tellurium with water: $TeCl_4 + 3H_2O = 4HCl + H_2TeO_3$. *β.* It may also be precipitated from tellurite of potassium or sodium, by adding nitric acid until a distinct acid reaction is produced. *γ.* Or, tellurium may be dissolved in nitric acid diluted to the sp. gr. of 1·25, and the solution, which is produced very rapidly or even violently, be poured, after the lapse of not more than a few minutes, into an excess of water, which will determine its precipitation. By any of these processes, tellurous acid is obtained as a somewhat bulky precipitate which, when dried over oil of vitriol, appears as a light white earthy mass having a bitter metallic taste. It is slightly soluble in water, especially when recently precipitated. It is soluble both in alkalies and acids, the nitric acid solution alone being unstable. Sulphurous anhydride, zinc, phosphorus, stannous chloride, and other reducing agents, precipitate metallic tellurium from the acidified solutions of tellurous acid. Like selenious acid, it is decomposed by sulphydric acid and sulphydrates, with formation of a dark brown sulphide of tellurium TeS_2, which dissolves readily in excess of alkaline sulphydrate to form a sulphotellurite $K_2TeS_3.2K_2S$.

(194) **Tellurites.**—Tellurous acid H_2TeO_3, is a hydrate in which the acid and basic tendencies are nearly balanced; or, in other words, the tellurium of the compound can replace the hydrogen of an acid to form salts of tellurium, and the hydrogen of the compound can be replaced by the basylous metals to form metallic tellurites, thus: —

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ACIDS.	SALTS OF TELLURIUM.		TELLURITES.	
H_2SO_4	$Te''''(SO_4)_2$	sulphate.	H_2TeO_3	tellurous acid.
HNO_3	$Te''''(NO_3)_4$	nitrate.	K_2TeO_3	tellurite of potassium.
$H_2C_2O_4$	$Te''''(C_2O_4)_2$	oxalate.	$KHTeO_3$	acid tellurite.
HCl	$Te'''' Cl_4$	chloride.	$KHTeO_3$, H_2TeO_3	quadritellurite.

Neutral tellurite of potassium is made by fusing tellurous acid or anhydride, and carbonate of potassium, in atomic proportions. It occurs as a crystalline mass, soluble in cold water, more readily in hot. The anhydro-bitellurite is made in the same manner, with two proportions of tellurous acid. It dissolves in hot water, forming the acid tellurite, which may be crystallised therefrom; but, by cold water, it is resolved into neutral tellurite which dissolves, and acid quadritellurite which precipitates. This last salt, like borax, is remarkable for the intumescence it undergoes when heated, prior to the production of a transparent glass. The tellurites of potassium, sodium, and ammonium are readily soluble in water; those of barium, strontium, and calcium sparingly soluble; the rest insoluble. Solutions of tellurites have a metallic taste, and are decomposed by the carbonic acid of the air. The majority of the salts are fusible, and, after fusion, crystalline. When ignited with fixed alkaline-carbonate and charcoal, they generally become converted into telluride of alkali-metal, which forms a port-wine coloured solution with water. Heated with charcoal, in the reducing blow-pipe flame, they yield tellurium, which burns with a green colour and deposits a white incrustation. Nearly all the tellurites dissolve in strong chlorhydric acid, forming yellow solutions, apparently of tetrachloride of tellurium, from which an excess of water precipitates tellurous acid.

Telluric Anhydride, Acid, and Salts.

(195) Telluric Anhydride. *Sym.* TeO_3; *p. n.* 177.—This compound is obtained by heating hydrated telluric acid to a temperature below redness. It occurs as an orange-yellow mass, which is insoluble in hot or cold water, in hot chlorhydric and nitric acids, and in solutions of caustic alkali. When strongly heated, it gives off oxygen, and leaves tellurous anhydride as a white earthy powder.

(196) Telluric Acid. *Sym.* H_2TeO_4; *p. n.* 195.—By fusing tellurium or tellurous anhydride with nitre, tellurate of potassium is obtained. The solution of this salt, decomposed by a salt of barium, yields a precipitate of tellurate of barium, from which, by

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the action of sulphuric acid, telluric acid is set free. Hydrated telluric acid, $H_2TeO_4 . 2H_2O$, crystallises from its solution in fine hexagonal prisms. It has a metallic rather than an acid taste, and affects litmus but slightly. It loses its water of crystallisation at a little above 100°, and is then scarcely soluble in cold water, save by long digestion, but it is dissolved more rapidly by ebullition. From this solution the crystalline acid may be re-obtained.

(197) TELLURATES.—These are for the most part not well defined. There appear to be neutral salts M_2TeO_4, acid salts $MHTeO_4$, quadracid salts $MHTeO_4.H_2TeO_4$, besides several anhydro-salts, of which the quadritellurate of potassium is the most remarkable. This salt is obtained, among other processes, by heating to a temperature below redness, the acid tellurate of potassium, $KHTeO_4$, when it breaks up into water which is evolved, neutral tellurate of potassium which may be dissolved out, and anhydro-tellurate which remains undissolved as a yellow mass, insoluble in chlorhydric acid, and in nitric acid, save by prolonged ebullition: —

$$6KHTeO_4 = 2K_2TeO_4 + K_2TeO_4 . 3TeO_3 + 3H_2O.$$

With this exception, the tellurates dissolve readily in cold chlorhydric acid. These solutions are not yellow, like those of the tellurites, but colourless, and will bear any amount of aqueous dilution without precipitation. On boiling, they give off chlorine, become yellow, and precipitable by water, owing to the formation of tellurous acid. The acidulous solutions of tellurates and telluric acid, like those of the tellurites, are decomposed, though not very readily, by sulphydric acid, with precipitation of a sulphide; and, by reducing-agents, with precipitation of tellurium, though somewhat slowly, and frequently only on the application of heat. Tellurates at a red heat give off oxygen to form tellurites. Heated with charcoal and alkaline carbonate, or before the blowpipe *per se*, they behave like tellurites.

(198) SULPHIDES OF TELLURIUM. — There are two definite sulphides of tellurium, corresponding to the two oxides. The bisulphide TeS_2, is formed by the action of sulphydric acid on a tellurous salt, or on an acidified solution of a tellurite. It also results from exposing the solution of a sulphotellurite of alkali-metal to the air. It is a dark-brown or black substance, which at a moderate heat softens, and on cooling acquires a semi-metallic lustre. When strongly heated, it evolves sulphur. It combines with the sulphides of basylous metals to form sulphotellurites, which, when in a soluble crystalline state, always contain excess of

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alkaline sulphide, $M_2TeS_3.2M_2S$. The tersulphide of tellurium TeS_3, results from the slow action of sulphydric acid upon dilute solutions of telluric acid. It occurs in brown glistening flakes. The sulphotellurates, to which it gives origin by its union with basylous sulphides, have not been examined.

§ V.—The Oxygen Group of Elements.

(199) Oxygen, Sulphur, Selenium, Tellurium.—These four elements are characterised by the distinctive property of combining each with two atoms of hydrogen, to form analogous volatile compounds of a neutral or feebly acid character. One gaseous volume of the element unites with two gaseous volumes of hydrogen, to form two gaseous volumes of the compound, the condensation consequently amounting to one-third. Hence, when two volumes of sulphydric acid gas H_2S, for instance, are decomposed by an iron wire, heated to redness by the transmission of a galvanic current, the sulphur is absorbed by the iron, and two volumes of hydrogen remain, or the original bulk of gas is unaltered by the absorption of its sulphur: whereas, when two volumes of chlorhydric acid gas HCl, for instance, are decomposed by a red-hot iron wire, the chlorine is absorbed by the iron, and only one volume of hydrogen is left, or the original bulk of gas is reduced to one-half by the abstraction of its chlorine. Again, water is decomposed by electrolysis into one volume of oxygen and two of hydrogen, whilst chlorhydric acid is decomposed into one volume of chlorine and one of hydrogen. Chemical and physical evidence alike demonstrate that the atom, or smallest indivisible proportion, of water and its congeners, contains twice as much hydrogen as the atom, or smallest indivisible proportion, of chlorhydric acid and its congeners. The chemical correlations of water and sulphydric acid are very marked; while the sulphydric, selenhydric, and tellurhydric acids present the most complete analogy with one another, both in their chemical and in their physical properties. All three are highly offensive inflammable gases, having a sparing solubility in water, and forming slightly acid solutions, which are decomposed by exposure to air, with precipitation of their respective elements. They all result from, and are capable of effecting, similar reactions.

Sulphur, selenium, and tellurium exhibit a striking similarity and regular gradation of properties. Oxygen manifests a general resemblance to the other three terms, and appears to bear towards them much the same relation that fluorine bears to chlorine, bro-

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mine, and iodine. The atomic weights and vapour densities occur in sequence: —

S	32		
Se	79·5	mean = 80·1	$= \frac{240·5}{3}$
Te	129		
Sum	240·5	mean difference =	48?

The atomic weight of oxygen, or 16, is exactly half that of sulphur. Its specific gravity also, or 16, is exactly half that of sulphur vapour when taken at a high temperature. The atomic heats of all four elements, when in combination, are the same, and are frequently expressed by the number 6, or some close approximation thereto. The atomic heats of sulphur, selenium, and tellurium, when in the free state, are respectively 6·48, 6·62, and 6·06. The atomic volumes of sulphur and selenium in the solid state, are 101 and 103 respectively, or sensibly equal. The number for tellurium is 128, the want of relation being possibly due to a want of correspondence in allotropic condition. Corresponding compounds of sulphur, selenium, and tellurium are for the most part isomorphous. The isomorphism of the sulphates and seleniates in particular is very complete, as exemplified in the two following series of salts: —

$Ca_2SO_4 . 2H_2O$	$Ca_2SeO_4 . 2H_2O$
$KNiSO_4 . 3H_2O$	$KNiSeO_4 . 3H_2O$
$Na_2SO_4 . 10H_2O$	$Na_2SeO_4 . 10H_2O$
$KAl(SO_4)_2 . 12H_2O$	$KAl(SeO_4)_2 . 12H_2O$

The seleniate of sodium, moreover, is not only isomorphous with the corresponding sulphate, but, like that salt, presents the anomaly of having a maximum point of solubility far below the boiling point of its solution. The elements sulphur and selenium are probably isomorphous in one, if not in two systems; but they are heteromorphous with tellurium, which crystallizes in the rhombohedral system. The isomorphism of combined oxygen with sulphur is not well marked. The majority of metallic sulphides, however, crystallize in the regular system, and are so far isomorphous with the corresponding oxides. Moreover, the oxisulphate and thiosulphate of sodium, $Na_2SO_4 . 10H_2O$ and $Na_2S_2O_3 . 10H_2O$ respectively, are said to be isomorphous. The specific gravities of sulphur, selenium, and tellurium, 2·0, 4·3, and 6·2 respectively, are gradational. The same relation subsists between the fusing points of the three elements, 120°, 211·5°, and 500° respectively, and also between their boiling points. Tellurium

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represents the metal of the series: moreover, selenium is not altogether destitute of metallic characters, and serves to connect metallic tellurium with non-metallic sulphur.

Oxygen and sulphur, and in all likelihood selenium and tellurium also, unite with hydrogen and its representatives, in a second and probably in several other ratios: —

Cl_2S	H_2S	K_2S	Ba_2O	H_2O	Cl_2O
Cl_2S_2	H_2S_2	K_2S_2	Ba_2O_2	H_2O_2	„
		K_2S_3	K_2O_3	H_2O_3?	Cl_2O_3
		K_2S_4	„	„	Cl_2O_4
		K_2S_5			

The primary hydrides of sulphur, selenium, and tellurium, and the derivatives thereof, unite with oxygen in several corresponding proportions, as we have seen, to form analogous bodies. Either one or both of the hydrogen-atoms in these compounds may be replaced by protequivalent metal, or, in other words, the hydrides are bibasic: —

H_2S	H_2Se	H_2Te
Cl_2SO	Cl_2SeO	Et_2TeO
Cl_2SO_2	Cl_2SeO_2 ?	Cl_2TeO_2
H_2SO_3	H_2SeO_3	H_2TeO_3
H_2SO_4	H_2SeO_4	H_2TeO_4

The corresponding oxides, or anhydrides, of sulphur, selenium, and tellurium, agree in their formulæ, and manifest a close resemblance in their chemical properties: —

SO_2	SeO_2	TeO_2
SO_3	SeO_3	TeO_3

They all react with water to form corresponding bibasic acids. The sulphurous, selenious, and tellurous anhydrides are readily volatile; while the sulphuric, selenic, and telluric anhydrides are decomposed at a red heat, with liberation of oxygen. The sulphurous, selenious, and tellurous acids are immediately decomposed by sulphydric acid, with precipitation of sulphides corresponding to the anhydrides; but the sulphuric, selenic, and telluric acids are either not affected, or but very slowly affected, by the reagent, and are indeed extremely stable at ordinary temperatures. Thus, their solutions dissolve zinc with simple displacement of hydrogen; whereas the sulphurous, selenious, and tellurous acids are reduced by the action of the metal.

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The number and variety of analogous compounds to which oxygen and sulphur give origin is very great: —

Carbonate of sodium	Na_2CO_3	Na_2CS_3	Sulphocarbonate of sodium.
Ether . . .	$C_4H_{10}O$	$C_4H_{10}S$	Sulphide of ethyl.
Cyanate of potassium	CNKO	CNKS	Sulphocyanate of potassium.
Selenious oxide .	SeO_2	SeS_2	Selenious sulphide.
Nitric oxide . .	N_2O_2	N_2S_2	Nitric sulphide.
Oxisulphide of antimony	Sb_2OS_2	Sb_2S_3	Tersulphide of antimony.
Antimoniate of sodium	Na_3SbO_4	Na_3SbS_4	Sulphantimoniate of sodium.
Phosphate of potassium	K_3PO_4	K_3PO_3S	Sulphoxiphosphate of potassium.

Very many of these sulphur-compounds can be represented by corresponding selenium and tellurium compounds: —

CNKO	Oxycyanate.	$C_4H_{10}O$	Ether.
CNKS	Sulphocyanate.	$C_4H_{10}S$	Sulphide of ethyl.
CNKSe	Selenocyanate.	$C_4H_{10}Se$	Selenethyl.
		$C_4H_{10}Te$	Tellurethyl.

(200) The relations of this group to the preceding halogen group are not very well marked. Chlorine is by equivalent substitution the representative of hydrogen, but, save in binary compounds, we know of few indisputable instances of the direct displacement of hydrogen or chlorine by oxygen or sulphur. We are, however, acquainted with a considerable number of bodies, which may be conceived as arising from such a substitution, two atoms of chlorine or hydrogen being represented by one atom of oxygen or sulphur, thus: —

Alcohol	C_2H_6O	$C_2H_4O_2$	Acetic acid.
Chloride of triethylstibine	$SbEt_3Cl_2$	$SbEt_3S$	Sulphide of triethylstibine.
Pentachloride of phosphorus	PCl_5	PCl_3O	Oxichloride of phosphorus.

Moreover, we meet with a very great number of corresponding oxides and chlorides, which contain respectively the same number of atoms of oxygen and chlorine, but in which the ratio thereunto of the other elements is as two to one, thus: —

Chloride of potassium .	KCl	K_2O	Oxide of potassium.
Terchloride of arsenic .	$AsCl_3$	As_2O_3	Arsenious anhydride.
Pentachloride of phosphorus	PCl_5	P_2O_5	Phosphoric anhydride.
Chloride of cuprosum .	Cu_2Cl	Cu_4O	Red oxide of copper.

The oxide and chloride of cuprosum are isomorphous with each other in the regular system. Moreover, iodine and sulphur both crystallise in the right prismatic system, as acute rhombic octahedrons. The metal manganese serves in a curious manner to

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associate the members of the first and second groups. We find this element at one time simulating chlorine, and at another time simulating sulphur, corresponding sulphates and manganates, and perchlorates and permanganates respectively, being isomorphous with one another: —

Perchlorate of potassium .	$KClO_4$	K_2SO_4	Sulphate of potassium.
Permanganate of potassium	KMn_2O_4	$K_2Mn_2O_4$	Manganate of potassium.

Sulphuric acid is the representative on the sulphur series of perchloric acid on the chlorine series. Each contains one atom of the radicle which gives the special character to the acid, in the one case chlorine, in the other sulphur. Each contains also four atoms or volumes of oxygen; but whereas perchloric acid contains only one atom or volume of hydrogen, sulphuric acid contains two atoms or two volumes. And this difference in composition leads to a marked difference in the properties of the two acids. Perchloric acid $HClO_4$, has only one atom of hydrogen that can be replaced. Hence it forms only one description of salt, such, for instance, as perchlorate of potassium $KClO_4$, and only one description of ether, such, for instance, as perchloric ether $EtClO_4$. But sulphuric acid H_2SO_4, has two hydrogen atoms that can be replaced. Hence it can form an acid salt $KHSO_4$, a neutral salt K_2SO_4, a double salt $KNiSO_4$, an acid ether $EtHSO_4$, a neutral ether Et_2SO_4, a double ether $EtMeSO_4$, and an ethylic salt $EtKSO_4$.

The peroxide and persulphide of hydrogen are binary molecules HO.HO and HS.HS respectively. HO is not, however, in any way comparable with HCl, the latter formula representing an entire, the former a hemi-molecule. HO presents several of the properties of Cl, and in very many reactions is capable of being exchanged for Cl, as has been already observed. For purposes of illustration, especially when comparing hydrates with chlorides, it is often advantageous to consider HO as occupying the place of a halogen, thus: $(CH_3)Cl$, chloride, and $(CH_3)HO$, hydrate of methyl.

(201) In comparing water with chlorhydric acid, we observe that, whereas in chlorhydric acid the displacement of the hydrogen must be effected at one stage only, in water the displacement can be effected at two stages. Thus, from chlorhydric acid HCl, we can obtain only chloride of sodium NaCl; whereas from water H_2O we can obtain first hydrate of sodium NaHO, and then oxide of sodium Na_2O. If we represent water by the ternary formula $\left.\begin{matrix}H\\H\end{matrix}\right\}O$,

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the propriety of representing similarly constituted molecules on the same type is self-evident, thus: —

$$\left.\begin{matrix}K\\H\end{matrix}\right\}O,\quad \left.\begin{matrix}K\\K\end{matrix}\right\}O,\quad \left.\begin{matrix}K\\Cl\end{matrix}\right\}O,\quad \left.\begin{matrix}H\\Cl\end{matrix}\right\}O,\quad \left.\begin{matrix}Cl\\Cl\end{matrix}\right\}O,\quad \left.\begin{matrix}K\\H\end{matrix}\right\}S,\quad \left.\begin{matrix}K\\K\end{matrix}\right\}S,\quad \left.\begin{matrix}Cl\\Cl\end{matrix}\right\}S,\ \&c.$$

But bodies of a much more complex character than any of those above represented are advantageously referred to the water type, when we have regard only to those reactions of the bodies which simulate the reactions of water and of its derivatives by elementary substitution. Alcohol and nitric acid, for instance, can undergo a variety of reactions to which the decompositions of water afford no parallel whatever. But they are also capable of undergoing very many reactions precisely similar to those which water undergoes by similar treatment; and, when regard is had only to this last class of reactions, as exemplified below, it is found very convenient to formulate the bodies on the water type, thus: —

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O + Na = \left.\begin{matrix}Na\\H\end{matrix}\right\}O + H \qquad 3\left|\left.\begin{matrix}H\\H\end{matrix}\right\}O + PCl_3 = H_3PO_3 + 3HCl\right.$$

$$\left.\begin{matrix}H\\NO_2\end{matrix}\right\}O + Na = \left.\begin{matrix}Na\\NO_2\end{matrix}\right\}O + H \qquad 3\left|\left.\begin{matrix}H\\NO_2\end{matrix}\right\}O + PCl_3 = H_3PO_3 + 3NO_2Cl\right.$$

$$\left.\begin{matrix}H\\C_2H_5\end{matrix}\right\}O + Na = \left.\begin{matrix}Na\\C_2H_5\end{matrix}\right\}O + H \qquad 3\left|\left.\begin{matrix}H\\C_2H_5\end{matrix}\right\}O + PCl_3 = H_3PO_3 + 3C_2H_5Cl\right.$$

In accordance with this convention, all monatomic alcohols, ethers, oxacids and their salts may be formulated on the type of one atom of water $\left.\begin{matrix}H\\H\end{matrix}\right\}O$. It is obvious that each or either atom of hydrogen in the type can only be displaced by a grouping or element which may be represented by x' or $_{,,}x_2$.

Nitric acid.	Nitric anhydride.	Nitric ether.	Nitrate potassium.	Mercurous nitrate.
$\left.\begin{matrix}(NO_2)'\\H'\end{matrix}\right\}O$	$\left.\begin{matrix}(NO_2)'\\(NO_2)'\end{matrix}\right\}O$	$\left.\begin{matrix}(NO_2)'\\(C_2H_5)'\end{matrix}\right\}O$	$\left.\begin{matrix}(NO_2)'\\K'\end{matrix}\right\}O$	$\left.\begin{matrix}(NO_2)'\\{}_{,,}Hg_2\end{matrix}\right\}O$
Alcohol.	**Ether.**	**Ethylate methyl.**	**Ethylate potassium.**	**Mercaptan.**
$\left.\begin{matrix}(C_2H_5)'\\H'\end{matrix}\right\}O$	$\left.\begin{matrix}(C_2H_5)'\\(C_2H_5)'\end{matrix}\right\}O$	$\left.\begin{matrix}(C_2H_5)'\\(CH_3)'\end{matrix}\right\}O$	$\left.\begin{matrix}(C_2H_5)'\\K'\end{matrix}\right\}O$	$\left.\begin{matrix}(C_2H_5)'\\H'\end{matrix}\right\}S$

In a similar manner all biatomic compounds, such as hydrates, oxides, alcohols, ethers, oxacids, and their salts, may be formulated on the type of the double atom of water $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$, one pair of the hydrogen atoms being displaced by x'', and the other pair by x'', or x'_2, or $_{,,}x_4$.

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Sulphuric acid. $\left.\begin{matrix}(SO_2)''\\H_2\end{matrix}\right\}O_2$

Glycol. $\left.\begin{matrix}(C_2H_4)''\\H_2\end{matrix}\right\}O_2$

Carbonic acid. $\left.\begin{matrix}(CO)''\\H_2\end{matrix}\right\}O_2$

Potassium acid-sulphate. $\left.\begin{matrix}(SO_2)''\\KH\end{matrix}\right\}O_2$

Glycol-monacetin. $\left.\begin{matrix}(C_2H_4)''\\H(C_2H_3O)'\end{matrix}\right\}O_2$

Potassium acid carbonate. $\left.\begin{matrix}(CO)''\\KH\end{matrix}\right\}O_2$

Potassium sulphate. $\left.\begin{matrix}(SO_2)''\\K_2\end{matrix}\right\}O_2$

Glycol-diacetin. $\left.\begin{matrix}(C_2H_4)''\\(C_2H_3O)_2'\end{matrix}\right\}O_2$

Potassium carbonate. $\left.\begin{matrix}(CO)''\\K_2\end{matrix}\right\}O_2$

Sulphethylic acid. $\left.\begin{matrix}(SO_2)''\\H(C_2H_5)'\end{matrix}\right\}O_2$

Stannous hydrate. $\left.\begin{matrix}Sn''\\H_2\end{matrix}\right\}O_2$

Oxalic acid. $\left.\begin{matrix}(C_2O_2)''\\H_2\end{matrix}\right\}O_2$

Potassium sulphethylate. $\left.\begin{matrix}(SO_2)''\\K(C_2H_5)'\end{matrix}\right\}O_2$

Stannous oxide. $\left.\begin{matrix}Sn''\\Sn''\end{matrix}\right\}O_2$

Oxalethylic acid. $\left.\begin{matrix}(C_2O_2)''\\H(C_2H_5)'\end{matrix}\right\}O_2$

Ethylic sulphate. $\left.\begin{matrix}(SO_2)''\\(C_2H_5)_2'\end{matrix}\right\}O_2$

Stannous sulphate. $\left.\begin{matrix}(SO_2)''\\Sn''\end{matrix}\right\}O_2$

Ethylic oxalate. $\left.\begin{matrix}(C_2O_2)''\\(C_2H_5)_2'\end{matrix}\right\}O_2$

All triatomic compounds also, such as hydrates, oxides, alcohols, ethers, oxacids and their salts, may be formulated on the type of the treble atom of water $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$, one set of hydrogen atoms being displaced by x''', or $(xx)'''$, and the other set by x''', or $(xx)'''$, or $x''+x'$, or x'_3, or $_{,,}x_6$.

Phosphoric acid. $\left.\begin{matrix}(PO)'''\\H_3\end{matrix}\right\}O_3$

Glycerin. $\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3$

Hydrate of bismuth. $\left.\begin{matrix}Bi'''\\H_3\end{matrix}\right\}O_3$

Phosphoric anhydride. $\left.\begin{matrix}(PO)'''\\(PO)'''\end{matrix}\right\}O_3$

Monacetin. $\left.\begin{matrix}(C_3H_5)'''\\H_2(C_2H_3O)'\end{matrix}\right\}O_3$

Oxide of bismuth. $\left.\begin{matrix}Bi'''\\Bi'''\end{matrix}\right\}O_3$

Stannous phosphate. $\left.\begin{matrix}(PO)'''\\HSn''\end{matrix}\right\}O_3$

Diacetin. $\left.\begin{matrix}(C_3H_5)'''\\H(C_2H_3O)_2'\end{matrix}\right\}O_3$

Ferric hydrate. $\left.\begin{matrix}(Fe_2)'''\\H_3\end{matrix}\right\}O_3$

Potassium monacid-phosphate. $\left.\begin{matrix}(PO)'''\\HK_2\end{matrix}\right\}O_3$

Triacetin. $\left.\begin{matrix}(C_3H_5)'''\\(C_2H_3O)_3'\end{matrix}\right\}O_3$

Ferric phosphate. $\left.\begin{matrix}(PO)'''\\(Fe_2)'''\end{matrix}\right\}O_3$

Phosphethylic acid. $\left.\begin{matrix}(PO)'''\\H_2(C_2H_5)'\end{matrix}\right\}O_3$

Glycerin-oxalate. $\left.\begin{matrix}(C_3H_5)'''\\H(C_2O_2)''\end{matrix}\right\}O_3$

Mercurous phosphate. $\left.\begin{matrix}(PO)'''\\{}_{,,}Hg_6\end{matrix}\right\}O_3$

Ethylic phosphate. $\left.\begin{matrix}(PO)'''\\(C_2H_5)_3'\end{matrix}\right\}O_3$

Glycerin-phosphate. $\left.\begin{matrix}(C_3H_5)'''\\(PO)'''\end{matrix}\right\}O_3$

Potassium sulphoxiphosphate. $\left.\begin{matrix}(PS)'''\\K_3\end{matrix}\right\}O_3$

In a similar manner, tetratomic and pentatomic compounds may be formulated on the types of four and five atoms of water respectively.

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CHAP. IV.

(202) ELEMENTS of which the single atoms unite respectively with three atoms or volumes of hydrogen, or of its representative, chlorine; namely, nitrogen, phosphorus, arsenic, antimony, and bismuth. The single atom of any one of these elements is usually equivalent to three atoms of a halogen or of hydrogen.

§ I. NITROGEN.

Symbol, N; *Proportional number*, 14; *Density*, 14; *Atomic volume*, □.

(203) Nitrogen exists abundantly in an uncombined state in the atmosphere, which is a mechanical mixture, consisting volumetrically of about 78 per cent. of nitrogen, 20·5 per cent. of oxygen, 1·5 per cent. of aqueous vapour, and ·05 per cent. of carbonic anhydride, with traces of several other gases and vapours. Though very inactive in the free state, nitrogen enters into the constitution of most interesting and important compounds. With hydrogen it forms ammonia; with hydrogen and oxygen, nitric acid; with carbon, cyanogen; with carbon, hydrogen, and frequently other elements in addition, a whole host of bodies, known as the natural and artificial alkaloids, such, for instance, as quinine, strychnine, aniline, &c. Moreover, the majority of organic colouring matters contain nitrogen, which is also an essential constituent of the proximate animal and vegetable principles, known as albumin, fibrin, casein, gelatin, &c. Nitrogen was discovered by Rutherford in 1772. Lavoisier subsequently ascertained that atmospheric air was composed of oxygen and nitrogen gases, the latter of which he called azote, from its incapability of supporting life (ἀ ζωή). Chaptal afterwards gave it the name nitrogen, from its entering into the composition of nitre, nitric acid, &c.

(204) Many chemical reagents have the property, either at ordinary or increased temperatures, of completely abstracting oxygen, aqueous vapour, and carbonic anhydride from the atmosphere, and consequently of leaving the nitrogen in an unmixed or pure state. The carbonic anhydride is generally absorbed by hydrate of calcium (slaked lime), or by hydrate of potassium used

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sometimes in the solid form, but most frequently in the state of concentrated solution. The aqueous vapour may be removed by quicklime, hydrate of potassium, or chloride of calcium, used in the solid state; or by oil of vitriol used either in the liquid state, or absorbed into fragments of pumice. Among the many reagents by which oxygen may be abstracted, the principal are: phosphorus, which acts slowly at ordinary temperatures, rapidly when ignited; finely-divided metallic copper or iron, at a red-heat; copper, moistened either with ammonia or an acid, chlorhydric or sulphuric, for instance; moist iron filings, whether or not mixed with sulphur; certain sulphides or sulphydrates, those of copper, iron, potassium and sodium, for instance; moist nitric oxide gas, which unites with the oxygen to form nitrous and nitric acids removable by washing with water, and leaves an excess of reagent removable by solution of green vitriol; alkaline solutions of the pyrogallates; moist charcoal or sawdust; also, living animals,—snails, very completely.

a. Nitrogen gas is most readily obtained from the atmosphere by one or other of the following processes: (*a.*) By floating a small capsule, containing one or two pieces of dried phosphorus, on water, then igniting the phosphorus, and covering it with a large glass receiver dipping into the water. After thoroughly washing the residual gas to remove the fumes of phosphorous and phosphoric acids, the nitrogen is left, contaminated only with aqueous vapour and a trace of carbonic anhydride. Or, a few sticks of unignited phosphorus may be left in contact with a confined bulk of air for some hours, whereby the oxygen is gradually absorbed. (*b.*) Air from a gasholder may be driven over fragments of caustic potash to absorb the carbonic anhydride and aqueous vapour, and then over red-hot metallic copper obtained in a finely-divided state by reducing the oxide in a current of hydrogen. (*c.*) Air from a gasholder may be passed through a large bottle filled with a mixture of moistened sawdust and precipitated oxide of iron which has been converted into sulphide of iron by a current of sulphydric acid gas. After its transit through this vessel, the air, deprived almost entirely of its oxygen, should be passed through a frame of four U-tubes, the first two containing solution of pyrogallate of potassium in caustic alkali, to absorb the carbonic anhydride and residual oxygen; the last two containing oil of vitriol, to absorb the aqueous vapour. This is a very convenient method in practice, as the sulphide of iron vessel may be restored to efficient action, an indefinite number of times, by the passage of sulphydric gas through it.

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β. Nitrogen may also be obtained in the free state by the decomposition of its chemical combinations with oxygen and hydrogen. (*a.*) Solution of nitrite of ammonia when boiled, breaks up into water and nitrogen, thus: $NH_4NO_2 = 2H_2O + N_2$. But nitrite of ammonia being a difficult salt to prepare, it is preferable to substitute for it in practice a mixture of sal-ammoniac and nitrite of potassium: —

$$NH_4Cl + KNO_2 = KCl + 2H_2O + N_2.$$

The gas obtained in either of these ways is perfectly pure. The nitrite of potassium solution may be obtained by passing nitrous anhydride, evolved from starch and nitric acid, into solution of hydrate of potassium, sp. gr. 1·38, until it acquires a decided acid reaction, when it is to be neutralised with more of the hydrate. This solution undergoes no change by keeping, and, when required to yield nitrogen, is to be mixed with three times its volume of a concentrated solution of sal-ammoniac. (*b.*) Nitrate of ammonia and sal-ammoniac may also be made to yield a supply of nitrogen, by heating them together in the dry state, and absorbing the resultant chlorine with slaked lime or caustic potash, thus: —

$$2NH_4NO_3 + NH_4Cl = N_5 + Cl + 6H_2O.$$

(*c.*) Nitrogen may also be obtained from nitrate of ammonia by dipping a piece of metallic zinc into the fused salt. (*d.*) Or it may be procured by saturating oil of vitriol with nitric oxide gas, adding sulphate of ammonia, and heating to a temperature of 130°. (*e.*) Or, by passing chlorine gas through solution of ammonia, taking care to keep the ammonia in considerable excess, and washing the liberated nitrogen with sulphuric acid to remove any adhering ammonia: —$4NH_3 + Cl_3 = N + 3NH_4Cl$. (*f.*) Or, by gently heating flesh, &c., in dilute nitric acid, and passing the resulting gas through solution of green vitriol to absorb any nitric oxide.

(205) Nitrogen is a colourless uncondensable gas, lighter than atmospheric air in the proportion of 97·13 to 100. It is tasteless, inodorous, and without any action on vegetable colours. It is sparingly soluble in water, 100 cubic inches of which, at 15°, dissolve only 1¼ cubic inches of nitrogen. It is incombustible, and does not support the combustion of ordinary combustibles. It does not support respiration; but, having no special action of its own upon the system, may be breathed for a time with impunity. It seems to be harmful only by preventing the inspiration of oxygen; for, mixed with oxygen, it is of course breathed constantly in ordinary

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respiration. As regards the allied processes of combustion and respiration, its function in the atmosphere appears to be merely that of a diluent, preventing the rapid action that the unmixed oxygen would otherwise effect. The metals titanium, tantalum, tungsten, and probably a few others, combine with, and even burn in nitrogen; but, save in these instances, free nitrogen manifests very slight chemical activity. When a long series of electric sparks is passed through a mixture of nitrogen and oxygen gases, standing over a solution of caustic alkali, combination slowly takes place, with formation of nitrate of alkali-metal. Traces of nitric acid and nitrate of ammonia also result from burning hydrogen gas, mixed with some nitrogen, in an atmosphere of oxygen or air. Moreover, nascent hydrogen can unite with free nitrogen to form ammonia. When nitrogen or air is passed over an ignited mixture of baryta and charcoal, cyanide of barium is produced:—

$$Ba_2O + N_2 + C_3 = 2BaCN + CO.$$

And when steam is passed over the cyanide of barium, heated to 300°, it is decomposed, with liberation of ammonia. The typical reaction is $BaCN + 2H_2O = BaHCO_2 + NH_3$; but other products, as well as formate of barium, are formed in the actual process. In several poly-hydrogenetted or chlorinetted compounds, one atom of nitrogen has been made indirectly to displace three atoms of hydrogen or chlorine.

Atmospheric Air.

(206) The air consists of free nitrogen and oxygen gases mixed in an almost invariable proportion, together with minute but variable quantities of aqueous vapour, carbonic acid or anhydride, ammonia, carburetted hydrogen, and probably other aëriform substances. The general composition of the atmosphere was first demonstrated by Lavoisier in 1777. A definite volume of air was acted upon by boiling mercury for many successive days, until its oxygen was entirely absorbed by the metal. The residual gas, or nitrogen, was then measured, and found to constitute about four-fifths of the whole. The oxygen was afterwards separated from the mercurial calx, by heating it to a temperature approaching that of redness, and found to measure about one-fifth of the original quantity of air experimented on. Almost simultaneously, Scheele discovered the composition of the atmosphere by absorbing its oxygen with solution of sulphide of potassium. He somewhat over-estimated, whereas Lavoisier had somewhat under-estimated, the proportion of oxygen present in the air. Priestley, who absorbed the oxygen by

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means of nitric oxide gas, considered its amount to be very variable; but Cavendish, who employed the same reagent, though with much greater precautions, first ascertained, in the year 1781, that the ratio of oxygen to nitrogen in air was practically invariable, and that the volume of oxygen constituted 20·8 per cent. of the whole, a per centage which corresponds exactly with that deduced from the most accurate modern experiments.

(207) At the present day, the composition of the air may be determined, with very considerable precision, by absorbing its oxygen with a ball of moist phosphorus, or with an alkaline pyrogallate; but the most exact processes, those in fact by which its composition has been satisfactorily established, are the following: — *a.* Eudiometric analysis. To a known volume of air is added a somewhat smaller bulk of pure hydrogen, the amount of which is also carefully noted. The mixed gases are then exploded in the eudiometer by means of an electric spark, whereby the oxygen is condensed in the form of water. The amount of contraction, one-third of which represents the bulk of oxygen originally present, is then exactly measured; or, in other words, the formula for the determination of the oxygen is—

$$x = \frac{V + V' - V''}{3}$$

in which V = the volume of air, V′ the volume of hydrogen, and V″ the volume of mixed gases after the explosion. This method of analysis is applicable to very small quantities of air, and when performed with the eudiometrical apparatus of Bunsen, Regnault, Frankland, or Williamson, affords results of the greatest accuracy. Of course, the proper corrections have to be made which the respective instruments require for variations of pressure, temperature, and vapour tension. Regnault collected the air from different parts of the earth's surface, and at different elevations, in straight tubes drawn out to capillary terminations. By means of bellows, the air of any locality was blown through the tubes, which were then sealed at both ends with the blow-pipe flame. The quantities of air so collected could be preserved unchanged for an indefinite time, to be examined at leisure in the laboratory. By a very large number of eudiometric analyses, Regnault determined the ratios of oxygen and nitrogen in air to be as follows: —

	By volume.	By weight.
Oxygen	20·93	23·13
Nitrogen	79·07	76·87
	100·00	100·00

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β. Analysis by weight. The following is an outline of the process employed by Dumas and Boussingault: — A tube of hard glass, furnished at each extremity with a stop-cock, was filled with porous metallic copper, reduced from its oxide by ignition in a current of hydrogen. This tube was then exhausted of air and weighed. To one extremity was attached a vacuous flask of about four gallons capacity, which was also weighed. To the other extremity was attached a series of U-tubes and Liebig's bulb-tubes, those nearest the copper containing pumice soaked in oil of vitriol, and those most remote containing stick potash, or strong solution of potash. The copper in the tube being heated to redness, the stop-cocks were carefully opened, whereby a current of air was gradually drawn through the potash tubes in which it was deprived of its carbonic acid, through the oil of vitriol tubes in which it was deprived of its moisture, and through the heated copper tube in which it was deprived of its oxygen, so that nothing but nitrogen passed into the vacuous flask. On the termination of the experiment, the increase in weight of the flask and of the tube containing the copper gave the total weight of air experimented on, and the increase in weight of the tube containing the copper, after being again exhausted by the air-pump, gave the weight of the constituent oxygen absorbed. By experiments conducted in this manner, Dumas and Boussingault arrived at the following determination of the composition of air: —

	By weight.	By volume.
Oxygen	23·0	20·8
Nitrogen	77·0	79·2
	100·0	100·0

(208) The presence of moisture and carbonic acid or anhydride in the air is easily rendered evident. The exterior of a vessel containing ice or a freezing mixture speedily becomes covered with dew or frost; and deliquescent salts, such as nitrate of copper, chloride of calcium, &c., speedily liquefy by exposure to air. Moreover, oil of vitriol contained in open vessels will frequently double its weight in the course of a few days, by an absorption of water from the atmosphere. Again, when a current of air is transmitted through baryta-water, lime-water, or solution of basic acetate of lead, or when these liquids are merely exposed to the air, they become more or less quickly turbid from the formation of the insoluble carbonates of their respective metals. The determination of the amounts of these two constituents is effected by means of an aspirator, arranged so as to draw a measured quantity of air

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through a succession of weighed U-tubes, one series containing pumice and oil of vitriol to absorb the water, and another series containing potash to absorb the carbonic anhydride, together with a final sulphuric acid tube to retain any moisture withdrawn from the potash. The increased weight in the oil of vitriol series of tubes gives the weight of the moisture; and that of the potash tubes, with the appended sulphuric acid tube, the weight of the carbonic anhydride. The proportion of aqueous vapour present in the atmosphere is very variable. Its average amount in this country is taken at about 1·5 per cent. by volume. The carbonic anhydride in the open air amounts on the average to ·04 per cent., but it ranges freely from ·03 to ·06 per cent. by volume.

Pettenkofer has introduced a ready and very accurate method of estimating the proportion of carbonic acid present in the atmosphere. A determinate volume of air, about a gallon being sufficient for the purpose, is agitated with a known quantity of lime-water of a known strength. A portion of the lime is thereby precipitated by the carbonic acid or anhydride of the air, and the amount so precipitated is ascertained, by carefully noting the quantity of a standard solution of oxalic acid required to neutralise the excess of lime left unacted upon.

The quantity of moisture existing in the air may be ascertained, not only by the chemical process previously described, but also by means of instruments known as hygrometers. The wet-bulb hygrometer consists of a thermometer, the bulb of which is kept constantly moistened with water. Other things being equal, the amount of moisture present in the atmosphere determines the rate of evaporation from the surface of the bulb, which rate of evaporation determines the diminution of temperature recorded by the thermometer. The dew-point hygrometer, in its simplest form, consists of a thermometer, the bulb of which is partially wrapped in muslin. By moistening this muslin with ether, the temperature of the thermometer is reduced, and a deposit of dew gradually formed on the uncovered portion of the bulb. The degree of temperature at which this deposit is formed, and at which it disappears, or the dew-point, is carefully observed. The less the proportion of moisture in the air, the lower the dew-point, or the lower the degree of temperature to which that air must be reduced in orderto become saturated with the moisture it contains.

The proportion of ammonia in the air is far too small to allow of its detection by ordinary experiments. It may, however, be

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recognised with facility in rain-water, especially in that which has fallen after a drought, or which has constituted the early portion of a shower. By acidifying several gallons of rain-water and evaporating to dryness, a residue of ammoniacal salt is left, from which ammonia may be set free by the action of lime or potash. Lawes and Gilbert, from experiments made in the country, at Rothamstead, in 1853-4, found on the average that one grain of ammonia was contained in about fourteen gallons of rain-water. But the rain-water of towns yields a greater proportion of ammonia than that of the country. Thus Barral's estimation of ammonia in the rain which fell at Paris, during the last five months of the year 1851, was about $3\frac{1}{2}$ times as high as Lawes and Gilbert's estimation of that in the Rothamstead rain. Boussingault's results in town and country accord generally with those of Barral, and of Lawes and Gilbert respectively. The ammonia found in rain-water has evidently been washed out of the atmosphere. The determinations by different observers of the amount which usually exists therein are most discrepant. Ten million parts of air contain, according to Fresenius, about 1·3 parts of ammonia, and according to Gröger about 3·3 parts; but other observers fix the proportion either very much higher or very much lower.

The presence of light carburetted hydrogen in the atmosphere was suggested by Boussingault, who showed that air, freed from moisture and carbonic acid, yielded both these compounds by transmission over ignited oxide of copper; and that the ratio of carbon to hydrogen in the two was the same as that in marsh gas.

The atmosphere has also been found to contain traces of various other constituents. For instance, sulphurous acid, from the combustion of coal, is frequently met with in the air of large towns; and the rain-water of London and Manchester is said to have an invariably acid reaction in consequence of its presence. Sulphydric acid has also been met with in the air of some localities. Nitric acid, again, is not unfrequently recognisable in rain which has fallen during, or soon after, a thunder-storm. Rain-water collected during windy weather, in the neighbourhood of the sea, usually contains common salt, from the mechanical dispersion of fine spray through the atmosphere. The air seems also to contain habitually a trace of organic matter; for when a very dilute solution of nitrate of silver is agitated frequently with considerable volumes of air, and exposed to sunlight, a reddish violet turbidity, not due to chlorine or sulphur, is produced. Again, glass globes filled with ice, and suspended in different atmospheres, cause a condensation of mois-

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ture which not unfrequently becomes turbid, putrid, and ammoniacal. Angus Smith has devised a process for estimating the amount of this organic matter, by observing the bulk of air required to decolorise the test-measure of a standard solution of permanganate of potassium. It is very doubtful whether miasmata and contagious emanations are truly volatile. Graham has well observed that the "volatility of a body implies a certain simplicity of constitution and limit to the number of atoms in its integral particle, which true organic bodies do not appear to possess. It is more probable that matters of contagion are highly organised particles of fixed matter, which may find their way into the atmosphere, and remain for a time suspended in it." From the circumstances that a veil worn over the face is reputed to afford a protection against the influence of marsh miasmata, and that elevated situations in the neighbourhood of unhealthy localities are often quite free from disease, Boussingault also has suggested that contagious matters do not exist in the form of vapour, but as fine flakes or particles, which are heavier than air.

(209) Atmospheric air is a colourless, tasteless, inodorous, incondensable gas. Its specific gravity, as compared with that of hydrogen, is 14·44. According to Regnault, one litre of air, freed from aqueous vapour and carbonic acid, under a pressure of 760^{mm}*, and at the temperature 0°, weighs 1·293 grammes; or, under the same pressure, 100 cubic inches of the same air weigh 32·586 grains at 0° and 30·829 grains at 15·5°.† Under the same pressure, this same purified air, at 0°, is 770 times lighter than water at its point of maximum density.

Atmospheric air supports both respiration and combustion, by

* At 29·92 inches.

† At 60° Fahrenheit. Miller gives the following table:—"100 cubic inches of dry air weigh, at 60° F., and 30 inches Bar., calculating from the experiments of

	Grains.
Dumas and Boussingault . . .	31·086
Biot and Arago	31·074
Prout	31·117
Regnault	30·935"

The mean of these four determinations is 31·05 grains, corresponding closely with that of Biot and Arago, which best accords with the calculated density of a mixture of oxygen and nitrogen gases in the atmospheric proportions. A cubic foot of air at mean temperature and pressure weighs 537 grains according to Biot and Arago, 536·5 grains according to the mean, and 534·5 grains according to Regnault. It is 816 times lighter than water at the same temperature, and about 11,000 times lighter than mercury.

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virtue of the oxygen which it contains. Its chief chemical action, namely, that of an oxygenant, though for the most part very slowly exerted at ordinary temperatures, is nevertheless, from the immense mass of the atmosphere, capable of producing most extensive and important results. Moreover, the aqueous vapour in the atmosphere exerts a powerful influence in the chemical and mechanical disintegration of minerals, and in other ways.

The mean pressure of the atmosphere at the sea-level is equal to that of 760 millimetres of mercury. The density of the air decreases with its elevation, according to a geometrical progression. At a height of 3·4 miles it is reduced to one-half, and is continually halved for every additional 3·4 miles of ascent. Hence one-half the entire mass of the atmosphere lies within three miles and a half of the earth's surface, and three-fourths of it within seven miles. The atmosphere is probably limited in its extent, but is believed to have an appreciable density at a height of 45 miles. The pressure of the atmosphere varies in different places*, according to their elevation, latitude, &c., and varies at the same place from time to time, owing to the action of winds and of other more or less ill-determined causes. The temperature of the atmosphere also decreases with its altitude. In the lower strata, it diminishes one degree centigrade for every five or six hundred feet of ascent. Hence, in every latitude, there is met with, at a certain height, a stratum of perpetual congelation. The limit of perpetual snow in this country is about 6,000 feet, at the equator about 15,000 feet high. This decrease of temperature with elevation depends chiefly upon the expansion which ascending air undergoes, through being subjected to less pressure, whereby its sensible heat becomes absorbed. Moreover, the atmosphere is heated principally by contact with the earth's surface, solar heat being transmitted through air, especially dry air, with little or no loss by absorption. Local alterations of atmospheric temperature are the primary causes of winds, heated air from its expansion rising vertically, and cold air rushing horizontally to supply its place.

Vapour-tension being dependent upon temperature, a deposition of moisture from the air is consequent upon a diminution of its temperature. Warm air, saturated with aqueous vapour at the surface, becoming cooled by its ascent and consequent rarefaction,

* In this country, the mean pressure of the atmosphere at the sea-level is generally estimated to be that of fifteen pounds on the square inch of surface equal to the weight of a column of mercury 30 inches high, or of a column of water nearly 34 feet high, having the same area.

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deposits its moisture in the form of clouds. But this deposition of moisture is attended with a liberation of latent heat, whereby the residual air is left warmer than the surrounding atmosphere, above which it consequently rises, becoming simultaneously rarer, cooler, and dryer. A deposition of moisture is frequently caused by contact of moist air with the cool crust of the earth. This is especially instanced by dew, which is deposited only when the temperature of the earth's surface is lowered by free radiation. Moreover, the amount of rain, which falls in any spot, varies inversely with the height from the earth at which it is collected.

(210) From the uniformity of its composition at every time, in every place, and at every elevation, the mixture of oxygen and nitrogen gases, which constitutes the great bulk of the atmosphere, was formerly thought by some to be a chemical combination. This uniformity, however, is satisfactorily accounted for on other grounds, and the notion itself is opposed by very many considerations. The invariable composition of the atmosphere in every place is brought about by means of diffusion, or the property which fluids, and especially gaseous fluids, have to mix with one another. Hence mixed gases, of different densities, do not separate and form distinct layers arranged according to their densities; but, on the contrary, layers of different gases, superimposed on one another according to their densities, speedily undergo a mutual diffusion or admixture, until a complete uniformity of composition is established. Dalton expressed this law by saying that one gas was to another as a vacuum; or, in other words, in every mixture of gases, each gas expands to fill the entire space within which it is confined, and exerts the pressure corresponding to its elasticity in its expanded state. Hence the final results are the same, whether we introduce a given volume of the gas x into a vacuous space, or into the same space occupied by the gas y. In each case, the gas x expands to fill the entire space, and increases the total pressure by the elastic force which it exerts in its rarefied condition. Graham has shown experimentally that the rapidity of diffusion or intermixture varies inversely with the square roots of the specific gravities of the gases, a result quite in accordance with Dalton's law. Moreover, the constant action of more or less powerful and extensive winds and currents tends largely to maintain a uniform composition of the atmosphere throughout the world.

The invariable composition of the atmosphere from time to time depends upon its immense mass, and upon the balance of the functions of animal and vegetable life. The respiration of animals and

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the combustion of fuel withdraw oxygen from the atmosphere; but the total quantity of air thus spoiled in a twelvemonth, by the breathing of living beings and the burning of fuel, despite the enormous figures by which it must be expressed, is as nothing compared with the entire mass of the air; for, supposing the atmosphere had through its whole extent the same density which it possesses at the earth's surface, it would envelope the globe as an aërial layer of about five miles in thickness. Prevost calculated that the total respiration and combustion of 100 years would not diminish the quantity of oxygen in the air by $\frac{1}{7100}$ part, a proportion far too minute to be detected by analysis. But a special provision also exists, in the growth of vegetables, by which a permanently unaltered composition of the atmosphere is maintained. Growing vegetables, under the influence of sunlight, absorb the carbonic acid and water given out by the combustion of fuel and respiration of animals, retain the carbon and hydrogen in their tissues, and restore the oxygen back to the air. The balance of vegetal and animal functions is well seen in Warington's aquaria, where the animal thrives upon the excreta of vegetal life, and the vegetable upon the excreta of animal life, the oxygen absorbed by the one being evolved by the other, and the carbonic acid evolved by the one being absorbed by the other.

The following reasons are conclusive against the supposition that the oxygen and nitrogen of atmospheric air exist in chemical combination. The density of the atmosphere and its refractive power are the respective means which should result from a mere mixture of its constituents; and moreover, an artificial mixture of oxygen and nitrogen gases, in the proper proportions, has all the chemical and physical properties of atmospheric air. Unlike the constituents of a chemical compound, the oxygen and nitrogen of the air do not exist in atomic proportions. The ratio approximates indeed to that of four atoms of nitrogen to one of oxygen, but the variation therefrom is much too great to be accounted for by any error in analysis. The two gases are intermixed without any condensation; but the only recognised combinations of gases, in which no condensation occurs, are those in which the respective gases combine atom to atom, and in these cases the resulting compounds differ altogether in their properties from mere mixtures of their constituents. Moreover, the chemical characters of air differ remarkably from those of any known oxide of nitrogen, and from those which an oxide of nitrogen of similar composition might be expected to present. The oxygen of the atmosphere may be withdrawn therefrom

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by even the most feeble chemical agencies, precisely as it may from mixtures of oxygen with hydrogen or carbonic anhydride. Again, air dissolves in water, not as a definite compound having its own coefficient of solubility, but as a mixture of two gases having each a solubility of its own; so that the gas extracted from water consists of about one volume of oxygen and two of nitrogen, owing to the coefficient of absorption of oxygen being greater than that of nitrogen. Lastly, the ratio of oxygen to nitrogen in the atmosphere does not appear to be absolutely invariable. Bunsen found the per-centage of oxygen in the air of Marburg, collected on ten different days, and freed from moisture and carbonic anhydride, to vary from 20·840 to 20·973, the difference amounting to 0·133; whereas the error in analysis never exceeded 0·031 per cent. Frankland recently examined the air of Chamounix at a height of 3,000 feet, that of the Grands Mulets at a height of 11,000 feet, and that of the top of Mont Blanc at a height of 15,732 feet. The per-centages of oxygen in the purified airs were respectively 20·894, 20·802, and 20·963, the difference between the air of the Grands Mulets and that of the summit amounting to 0·161 per cent. Regnault's numerous experiments with specimens of air obtained from various places, and under the most diverse conditions, also showed that minute but sensible variations did exist in the proportions of oxygen present; and similar results have been obtained by Stas, Lewy, and others. Except in very special cases, however, the proportion of oxygen present varies only from 20·8 to 21·0 per cent. by volume. According to Dalton's theory of the constitution of mixed gases, the ratio of oxygen to nitrogen in the atmosphere should decrease with the elevation, inasmuch as each gas is subjected only to the pressure caused by its own density. But experiment has not confirmed this conclusion, probably because no examination has ever been made of air collected at an altitude above the influence of the great polar and equatorial currents. Thus Miller found the air collected by means of a balloon, at a height of 18,000 feet, to contain 20·88 per cent. of oxygen.

The total quantity of carbonic anhydride in free air varies in the ratio of two to one; but from the small proportion present at any time, the variability in its per-centage amount is much less even than in that of oxygen. The younger Saussure, from many hundred analyses of air, found the carbonic anhydride to vary from ·037 to ·062 per cent., with a mean of ·049. According to him, the proportion of carbonic anhydride in air collected near

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the surface is greater in summer than in winter, greater before than after rainfall, and greater in the night than in the day. He also observed that carbonic anhydride is more abundant in the air of elevated situations than in that of the plains, a result confirmed to some extent by Frankland, who found in air from the Grands Mulets ·111, and in that from the top of Mont Blanc ·061 per cent. of the gas, both determinations being considerably above the average. According to Lewy, the air over the sea contains much the same proportion of carbonic anhydride as the air of the land; but sea-air is decidedly richer by day than by night, both in carbonic anhydride and oxygen, owing probably to an evolution of dissolved gases from the heated surface of the ocean during the day. Generally speaking, however, an increased proportion of carbonic anhydride is accompanied by a decreased proportion of oxygen. The composition of air within doors may vary considerably from that of the external atmosphere; but, according to Roscoe, the proportion of carbonic anhydride cannot possibly exceed ·5 per cent., owing to the rapid interchange by diffusion which takes place when any approach is made to that ratio. He once found the air of a crowded schoolroom to contain ·330 per cent., and that of a crowded theatre ·321 per cent. of carbonic anhydride. He always found the distribution of carbonic anhydride to be very uniform within the same room. A confined atmosphere is rendered unwholesome, not by a consumption of its oxygen, but by an increase in the proportion of its carbonic anhydride, effected by the processes of respiration and combustion.

Ammonia.

Symbol, NH_3; *Proportional number*, 17; *Density*, 8·5; *Atomic volume*, □□.

(211) Small quantities of ammonia, in the form of some ammoniacal salt, are met with naturally under a variety of circumstances. Thus, chlorhydrate of ammonia has been recognised in the rock-salt of the Tyrol; native sulphate and chlorhydrate of ammonia have been found in volcanic neighbourhoods, and a native ammonia-alum in some parts of Bohemia. Traces of carbonate and nitrate of ammonia exist in the air, and consequently in rain-water. The sea and many natural waters also contain the chlorhydrate and other ammoniacal salts. Various clays and ochres, rust of iron, and indeed nearly all native peroxides of the metal, contain traces of ammonia. Ammoniacal salts exist in the

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juices of plants and in most animal fluids. The urine especially contains ammonia united with phosphoric, uric, and other acids. Guano also, which is the naturally dried excrement of sea-fowl, furnishes an important supply of ammonia for the agricultural purposes of this country. Camels' dung is said to contain chlorhydrate of ammonia, and is at any rate the source from which that salt was at one time obtained, by a process of sublimation first practised in Libya, near the temple of Jupiter Ammon, whence the name ammonia. Black, in 1756, distinguished between ammonia and its carbonate. Priestley, in 1774, discovered gaseous ammonia.

(212) The direct combination of hydrogen and nitrogen gases can be effected in a very imperfect manner only. The combustion of hydrogen, mixed with a small proportion of atmospheric air, is said to yield traces of nitrate of ammonia; and a mixture of hydrogen and nitrogen gases with some acid vapour, is said to yield an ammoniacal salt by the passage of electric sparks through it. But nascent hydrogen has the undoubted capability of uniting with nitrogen to form ammonia. Hence, during the electrolysis of water containing atmospheric air, a trace of ammonia is formed at the negative pole. Nearly all oxidations taking place in presence of air and moisture, give rise to the production of ammonia or its salts. A mass of moistened iron-filings, for instance, when exposed to the air, becomes oxidised, partly by the direct action of the atmosphere, partly by the decomposition of water, some of the hydrogen from which appears in the form of ammonia. The mutual reaction of zinc-filings, water, and air produces a similar result; and indeed the evolution of hydrogen, from any mixture of materials exposed to the air, is accompanied, to a greater or less extent, by the production of ammonia, either free or in combination. Ammonia is also a very frequent product of the reduction, by different processes, of oxidised compounds of nitrogen. Thus it is produced by the reaction of nitric oxide and sulphydric acid; by passing nitric oxide and hydrogen gases over red-hot porous materials; by adding a nitrite or nitrate to any mixture evolving hydrogen; by heating a nitrite or nitrate with an acid solution of stannous chloride, &c. &c. Ammonia results, moreover, from the decomposition, by water or hydrates, of the various compounds of nitrogen with chlorine, sulphur, phosphorus, carbon, boron, &c.; the cyanides, or carbo-nitrides, in particular, yielding ammonia by their reaction with steam at a high temperature. But the chief source of ammonia and its compounds is the decomposition, either by putre-

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faction or destructive distillation, of nitrogenous organic matter. Thus, solution of ammonia was originally obtained by Raymond Lully from putrefied urine, and was known as *spiritus animalis*. The putrefaction of non-nitrogenous organic matter, in the presence of air, that of starch paste for example, also produces traces of ammonia. The burning of bones in close vessels for the purpose of making animal charcoal, or bone-black, yields a large amount of ammoniacal liquor, which at one time formed the principal source from which the salts of ammonia were produced. The redistilled liquor constituted *spirits of hartshorn*. At the present time, the destructive distillation of coal in gasworks furnishes by far the largest supply of ammonia and its compounds. The gas liquor is distilled, neutralised with sulphuric acid, and the resulting sulphate of ammonia separated by evaporation and crystallisation. The nitrogen of most organic compounds may be completely converted into ammonia by igniting the substances with an excess of caustic alkali, a mixture of the hydrates of sodium and calcium, known as soda-lime, being generally employed for the purpose.

(213) Ammonia is almost always prepared by the action of caustic alkali, usually slaked lime, upon a salt of ammonia, usually sal-ammoniac: —

$$NH_3HCl + CaHO = CaCl + H_2O + NH_3.$$

The mixed substances in the state of powder or paste are heated in a flask or retort, and the evolved ammoniacal gas is transmitted through a large Woulfe's bottle, in which it can deposit moisture and any mechanical impurities. It may be collected either over mercury or by upward displacement; or it may be absorbed either by water, in which it is very soluble, or by certain metallic salts, chloride of silver for instance. From its solution in water, or from some of its compounds with metallic salts, free ammonia may be easily re-obtained by the application of a moderate heat. Indeed the readiest way of procuring gaseous ammonia consists in gently heating its strong aqueous solution, with or without the addition of solid chloride of calcium. The resulting gas may, if necessary, be dried by transmission over stick potash, or quicklime.

(214) Ammonia is an easily condensable gas, and may be obtained in the liquid state either by refrigeration or by pressure. The thoroughly dried gas, cooled down by means of ice and salt, is conveyed into a suitable tube surrounded by a freezing mixture of ice and chloride of calcium, whereby a temperature of $-40°$ is attained,

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and the gas liquefied; or chloride of silver, saturated with dry ammonia, is heated to a temperature of 112-20° in one limb of a sealed V-tube, and the liberated gas condensed in the other limb kept cool by ice. The chloride of silver on cooling re-absorbs the ammonia. By submitting liquid ammonia to the intense cold produced by the evaporation in vacuo of solid carbonic anhydride and ether, it may be solidified.

Solid ammonia is a colourless, transparent, crystalline substance, which melts at −75°. Liquid ammonia is a colourless, very mobile, and highly refractive fluid. Its sp. gr. is 0·73; it boils at − 34°; its tension at 0° = 4·44, and at 15·5° = 7 atmospheres. Gaseous ammonia is rather more than half as heavy as atmospheric air. It has a very pungent, exciting smell. Its attempted inspiration causes closure of the glottis, and produces inflammation of the mucous membrane of the air passages. Animals immersed in it speedily die. When considerably diluted, it may be breathed without marked inconvenience. It has a highly alkaline taste, and, even when perfectly dry, turns turmeric paper brown, violet, or rose paper green, brazil paper crimson, and red litmus paper blue.

Ammonia combines with, or is absorbed by, a great variety of compounds, including water, the alcohols, ethers, acids, anhydrides, chlorides of various radicles, and many metallic salts. In the presence of any volatile acid, chlorhydric or nitric for instance, it forms dense opaque white fumes, from the union of the two vapours, and consequent deposition of ammoniacal salt. The hydrogen of ammonia is capable of being displaced by chlorous and basylous elements, and by chlorous and basylous groupings. The basylous derivatives are for the most part capable, like ammonia itself, of uniting directly with acids and salts.

Ammonia is gradually decomposed into its elements by the transmission of a succession of electric sparks through it, two volumes of the gas being resolved into three volumes of hydrogen and one volume of nitrogen. The same decomposition is effected by passing the gas through a red-hot tube, filled with some finely-divided solid to facilitate the transference of heat.

Ammoniacal gas is very feebly combustible. A jet of ammonia burns when transmitted through the flame of a gas or spirit lamp, or even across the current of hot air proceeding from an argand burner; but it can only maintain its own combustion in oxygen gas or chlorine. A mixture of oxygen and ammonia, procured by passing a rapid current of oxygen through boiling solution of ammonia, burns readily with a characteristic greenish yellow flame.

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A mixture of oxygen and ammonia may also be exploded by the electric spark, but the products vary according to the relative proportions of the two gases. Ammonia is readily and under a great variety of circumstances oxidised into nitric acid. A jet of ammoniacal gas introduced into an atmosphere of chlorine, takes fire spontaneously and burns with a greenish-yellow flame, forming nitrogen and chlorhydric acid, a portion of which combines with some of the undecomposed ammonia. In a similar manner, chlorine gas passed into solution of ammonia forms chlorhydrate of ammonia and free nitrogen, with a portion of which it sometimes unites to form trichloride of nitrogen NCl_3. Bromine effects a reaction corresponding to that of chlorine. Iodine forms iodhydrate of ammonia and iodamine NHI_2. Dry ammonia passed over dry carbon heated to redness, produces cyanhydrate of ammonia and hydrogen: $C + 2NH_3 = NH_3HCN + H_2$. Potassium heated in ammonia displaces one-third of its hydrogen to form potassamine NH_2K. Sodium reacts in a similar manner, producing sodamine NH_2Na. The reactions of ammonia with various chlorides, ethers, anhydrides, acids and salts, will be referred to further on.

(215) Ammoniacal gas is instantaneously absorbed by water, and very rapidly by ice, which thereby liquefies. A flask of dry ammoniacal gas, opened under water, is frequently broken by the violent rush of liquid. According to Roscoe, one volume of water absorbs 1147 volumes of ammonia at 0°, and 783 volumes at 15°. The act of absorption is attended with a considerable development of heat, a great increase in bulk, and an obvious decrease in specific gravity. Two parts of water, saturated with ammonia at mean temperature and pressure, become more than three parts of solution both by weight and measure. The absorption of ammonia by water follows Dalton's law of pressures only at temperatures above 100°. Solution of ammonia is a colourless, transparent liquid, having a very pungent smell, a burning caustic taste, and strong alkaline reaction. Its specific gravity varies inversely with its concentration from ·850 to 1·000. Its boiling-point also varies inversely with its concentration. The ammoniacal gas is gradually expelled by heating the liquid, and at a temperature of 100° may be driven off entirely. A saturated solution of ammonia freezes at about −40° in shining flexible needles. Aqueous ammonia is largely used in the laboratory as a reagent. It dissolves many oxides and salts which are insoluble in water, the oxides of copper and cadmium, the chloride and phosphate of silver, for instance. Solution of ammonia is prepared on the manufacturing scale by

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heating sal-ammoniac with an equal weight of quicklime, slaked and made into a paste with water. The ammonia is passed first into a receiver, either empty or containing a little water or milk of lime, in which any mechanical or empyreumatic impurities may be deposited, and then into a series of large Woulfe's bottles containing the water to be saturated with the gas, and kept cool by immersion in water. Alcohol like water absorbs ammoniacal gas, with considerable expansion and evolution of heat. Ammonia is even more soluble in alcohol than in water. The specific gravity of this solution also varies inversely with the proportion of ammonia dissolved.

Derivatives of Ammonia.

(216) One or more of the hydrogen atoms in the single, double, or treble molecule of ammonia may be displaced by a halogen or a basylous metal to form bodies of the class represented below. Moreover, some or all of the hydrogon atoms may be displaced by basylous groupings to form amine bases, or by chlorous groupings to form amides of a more or less acid character.

NH_2K	Potassamine.	$NH_2(C_2H_5)'$	Ethylamine.
NHI_2	Diniodamide.	$NH(C_2H_5)'_2$	Diethylamine.
NCl_3	Trichloramide.	$N(C_2H_5)'_3$	Triethylamine.
NHg_3	Trimercuramine.	$N_2H_4(C_2H_4)''$	Ethylendiamine.
NZn_3	Trizincamine.	$NH_2(C_2H_3O)'$	Acetamide.
$NHPt''$	Platinamine.	$N_2H_4(SO_2)''$	Sulphodiamide.
N_2H_4Pt''	Platindiamine.	$N_3H_6(PO)'''$	Phosphotriamide.

Amine and amide compounds are formed by many different processes; among others by the reaction of ammonia upon various ethers, anhydrides, and chlorides, or their respective analogues. Benzamide, for example, may be made by treating benzoic ether, benzoic anhydride, or chloride of benzoyl, with ammonia, as shown below, and similarly in many other cases of the formation of amides, diamides or triamides, and of amines, diamines, or triamines.

$$\left.\begin{matrix}(C_2H_5)\\(C_7H_5O)\end{matrix}\right\}O + NH_3 = \left.\begin{matrix}(C_2H_5)\\H\end{matrix}\right\}O + NH_2(C_7H_5O)$$

$$\left.\begin{matrix}(C_7H_5O)\\(C_7H_5O)\end{matrix}\right\}O + 2NH_3 = \left.\begin{matrix}(C_7H_5O)\\NH_4\end{matrix}\right\}O + NH_2(C_7H_5O)$$

$$(C_7H_5O)\,Cl + 2NH_3 = NH_4\,Cl + NH_2(C_7H_5O).$$

The action of ammonia upon an anhydride is equivalent to its action upon an acid, with elimination of water, presently to be

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referred to. The metalamines will be described under the heads of their respective metals; and the compound amine bases and neutral and acid amides along with the chlorides and hydrates of their respective radicles.

(217) CHLORIDE OF NITROGEN. *Sym.* NCl_3; *p. n.* 120·5.— *a.* This highly explosive compound may be formed by filling a bottle, which has been carefully cleaned and freed from every trace of greasy impurity, with chlorine gas, and inverting it over a leaden dish containing a weak solution of some ammoniacal salt, one part of sal-ammoniac dissolved in twelve or fifteen parts of water being usually employed. The chlorine becomes gradually absorbed, while yellow oily drops of chloride of nitrogen form on the surface of the liquid and soon fall to the bottom: —

$$NH_4Cl + Cl_6 = 4HCl + NCl_3.$$

β. Or a small lump of sal-ammoniac may be suspended in an aqueous solution of hypochlorous acid, whereby the same compound is deposited: —

$$NH_4Cl + 3HClO = HCl + 3H_2O + NCl_3.$$

Chloride of nitrogen is a thin yellow oil, of sp. gr. 1·653. It volatilises readily in the air, giving off a peculiar penetrating odour. It is decomposed with a most violent though local explosion, when heated to nearly 100°, or when touched with any oil or fat, with turpentine, with phosphorus, and many other substances. It is decomposed without explosion by the chlorhydric, sulphydric, and sulphurous acids. By its reactions with these last substances its composition has been ascertained, though not with absolute certainty. The reaction with sulphurous acid is as follows: —

$$NCl_3 + 3H_2SO^3 + 3H_2O = NH_4HSO_4 + 2H_2SO_4 + 3HCl.$$

(218) DINIODAMIDE. *Sym.* NHI_2; *p. n.* 269.—This compound, familiarly known as iodide of nitrogen, may be obtained by digesting powdered iodine in strong aqueous ammonia. After some time the brown supernatant liquid may be poured off, and small quantities of the deposit placed on separate pieces of filtering paper to dry spontaneously in the air. Or an alcoholic solution of iodine may be added to strong aqueous ammonia, and the deposit collected on pieces of filtering paper as before: —

$$3NH_3 + I_4 = 2NH_4I + NHI_2.$$

Iodide of nitrogen forms a soft brownish-black powder. When

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moist it may be handled with impunity, but when dry the slightest friction or elevation of temperature causes it to explode with great violence. A portion allowed to fall from a table will frequently explode before it reaches the ground. It is decomposed quietly by the chlorhydric, sulphydric, and sulphurous acids. The reaction with sulphydric acid is as follows: —

$$NHI_2 + 2H_2S = NH_4I + HI + S_2.$$

Ammoniacal Salts.

(219) Ammonia has the property of uniting directly with acids to form well-defined neutral crystalline salts, known as ammonia salts, or salts of ammonium, the composition of a few of which is shown in the following table: —

$NH_3 . HCl$	Chlorhydrate of ammonia.
$NH_3 . HNO_3$	Nitrate of ammonia.
$NH_3 . H_2SO_4$	Acid sulphate of ammonia.
$2NH_3 . H_2SO_4$	Normal sulphate of ammonia.

Now the salts of ammonia correspond in many of their properties to metallic salts, particularly to salts of potassium, with which, indeed, they are frequently isomorphous; and by associating an atom of hydrogen from the acid, with each atom of ammonia in the salt, we are enabled to give to ammoniacal salts formulæ analogous to those of potassium- and other metallic salts; the molecular grouping NH_4, or ammonium, being looked upon as the representative of one atom of a prot-equivalent metal, thus: —

Chloride of potassium	KCl	$(NH_4)Cl$	Chloride of ammonium.
Nitrate of potassium	KNO_3	$(NH_4)NO_3$	Nitrate of ammonium.
Acid sulphate	$KHSO_4$	$(NH_4)HSO_4$	Acid sulphate of ammonium.
Normal sulphate	K_2SO_4	$(NH_4)_2SO_4$	Normal sulphate of ammonium.

Without assuming any acquaintance with the actual molecular arrangement of ammoniacal salts, it is found most convenient in practice, when comparing them with metallic salts, to consider them as salts of ammonium, and when comparing them with alkaloidal salts, and particularly when discussing their relations with the neutral and acid amides, to consider them as salts of ammonia. Generally speaking, it is a matter of indifference which nomenclature and notation are employed, save that the ammonium formulæ are usually rather the simplest. The salts of the amine bases may be represented in a corresponding manner. Thus chlorhydrate of ethylamine $NH_2(C_2H_5) . HCl$, may be expressed as a chloride of

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ethylammonium $NH_3(C_2H_5)Cl$, and iodethylate of triethylamine $N(C_2H_5)_3 . C_2H_5I$, as an iodide of tetrethylammonium $N(C_2H_5)_4I$. Similarly chlorhydrate of platosamine may be considered as a chloride of platosammonium NH_3PtCl, and iodomercurate of trimercuramine as an iodide of tetramercurammonium NHg_4I.

(220) The theory of ammonium derives considerable support from the very similar electrolytic effects obtainable with solutions of potassium- and ammonium-salts, whereby potassium- and ammonium-amalgams are respectively obtained. The production of ammonium-amalgam not only serves to demonstrate the existence of ammonium, but also indicates its metallic character, seeing that metals are the only bodies which can yield amalgams. Potassium-amalgam may be readily obtained from solution of chloride of potassium, by the weak current of a single cell having a few drops of mercury for its negative pole. The mercury gradually swells up to several times its bulk; and, if the current be transmitted thereto by means of a platinum wire, the wire becomes amalgamated through a considerable portion of its length, owing to the creeping up of the potassium-amalgam. When removed from the influence of the current, the amalgam of potassium is rapidly decomposed by water, with evolution of hydrogen and formation of a strongly alkaline solution. Now if chloride of ammonium be substituted for chloride of potassium, the only noticeable difference in the experiment is that the mercury swells up to a much greater extent. The platinum wire leading to the mercury becomes similarly amalgamated, and the separated amalgam undergoes rapid decomposition with water, evolving hydrogen and forming an alkaline solution. If the platinum wire, amalgamated at one end with the ammonium-amalgam, be itself used as the negative pole, the action still continues, and a bulky amalgam, containing so little mercury as to be lighter than the solution, is formed. This amalgam, when no longer conducting the current, is decomposed almost instantaneously by water, with evolution of hydrogen and formation of aqueous ammonia. Thus the potassium- and ammonium-amalgams seem to be identical in character; they are formed under the same circumstances, and their decompositions may be expressed in corresponding manners, hydrate of ammonium being regarded as the analogue of hydrate of potassium, thus: —

$$Hg_xK + H_2O = Hg_x + KHO + H$$
$$Hg_xNH_4 + H_2O = Hg_x + NH_4HO + H.$$

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When sodium-amalgam, made by dissolving sodium in mercury, is allowed to act upon a warm dilute solution of sal-ammoniac, a very bulky ammonium-amalgam is at once produced, having a spongy or pasty texture, a leaden colour, and metallic aspect. It contains a larger proportion of mercury than the electrolytic amalgam, than which it is somewhat more stable; but, by the action of water, it is eventually resolved into mercury, ammonia, and hydrogen. The amalgam of ammonium, when more slowly formed from sodium-amalgam, and cooled down considerably below 0°, may be obtained crystallised in cubes.

(221) The salts of ammonium are, for the most part, readily crystallizable, and are frequently isomorphous with the corresponding salts of potassium and sodium. They have a cooling saline taste, and, with the exception of the carbonates, are devoid of smell. All the salts, save those of coloured acids, are colourless. The normal salts of monobasic, bibasic, and tribasic acids are usually neutral, but some of them have a marked alkaline reaction like the corresponding salts of fixed alkali metals. Ammoniacal salts are freely soluble in water, less so in alcohol. The aqueous solutions of the salts, even those of strong monobasic acids, nitric and chlorhydric for instance, evolve ammonia during their evaporation by heat. Solutions of ammoniacal salts, when boiled with any metallic protoxide or prothydrate, are decomposed with evolution of ammonia:—

$$2NH_4NO_3 + Zn_2O = 2ZnNO_3 + H_2O + 2NH_3.$$

The presence of any ammoniacal salt in a liquid or solid, is usually ascertained by heating it for a short time with milk of lime or caustic potash, and holding in the vapour either a rod dipped in chlorhydric acid, whereby opaque white fumes of sal-ammoniac are formed, or a piece of moistened red litmus or turmeric paper, the characteristic alteration in the colour of which indicates the alkaline nature of the vapour. Ammoniacal vapour also produces a black stain on paper moistened with subnitrate of mercury, a blue stain on paper moisted with sulphate of copper, and a brown stain on paper moistened with chloride of manganese solution. When the quantity of ammonia evolved is too small to react with these tests, a portion of the liquid may be distilled with potash or lime, and the alkalinity of the distillate ascertained either by reddened litmus solution, or by a mixture of arsenious acid and nitrate of silver solutions, whereby a yellow turbidity of arsenite of silver is produced (Aikin). The phosphomolybdate of sodium gives, even with very dilute solutions of ammonium salts, a yellow precipitate, which is insoluble in mineral acids, but is not formed

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in presence of fixed organic acids or of free alkalis (Sonnenschein).* An alkaline solution of the potassium iodide of mercury gives with ammonium salts, or ammonia, a brown precipitate or turbidity, consequent upon the production of the iodide of tetramercurammonium $NHg_4I.H_2O$ (Nessler).† This is a very delicate and convenient test for traces of ammoniacal salts. The chlorhydric acid solution of bichloride of platinum gives with ammonium salts a yellow crystalline precipitate of ammonio-chloride of platinum NH_4PtCl_3, which is slightly soluble in water, insoluble in alcohol. Unlike the similar compound of potassio-chloride of platinum, this precipitate, when ignited, leaves a residue of pure platinum, not yielding a trace of any alkaline chloride to water. Excess of tartaric acid gives with neutral or alkaline solutions of ammonium salts, provided they are not too dilute, a white crystalline precipitate of acid tartrate of ammonium $C_4H_5(NH_4)O_6$, soluble in alkalis and in mineral acids. Unlike the similar compound of acid tartrate of potassium, this precipitate, when ignited, leaves a mass of charcoal devoid of any alkaline reaction. The compounds of ammonia with volatile acids are completely dissipated by heat, the hydracid salts being volatilised unchanged. The molecules of chloride, cyanide, and sulphydrate of ammonium have been found to yield four volumes of vapour The compounds of ammonia with fixed acids are decomposed by heat, giving off their ammonia with some or all of their water, and leaving residues of fixed acid or anhydride. The ammoniacal salts of reducible acids undergo a reduction by heat, with evolution of free nitrogen. In this manner the anhydro-bichromate of ammonium yields chromic oxide, water, and nitrogen, thus; —

$$(NH_4)_2Cr_4O_7 = Cr_4O_3 + 4H_2O + N_2.$$

(222) The intermediate effects of heat upon the monobasic, dibasic, and tribasic oxacid salts of ammonia, as illustrated below, are extremely interesting.

* Phosphomolybdate of sodium is prepared by igniting the precipitate of phosphomolybdate of ammonium, produced by adding molybdate of ammonium to solution of phosphate of sodium acidified with nitric acid. The ignited residue is moistened with nitric acid to oxidise any reduced molybdic acid, re-ignited, dissolved in carbonate of sodium; and the solution, acidified with chlorhydric acid, is preserved for use.

† This compound is obtained by adding iodide of potassium to solution of corrosive sublimate until the precipitate is almost redissolved. To the clear solution, caustic potash is then added, and the liquid so produced, after clarification by subsidence, is employed as the reagent.

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MONOBASIC.

$HClO_4 + NH_3 - H_2O = NH_2(ClO_3)$ Perchloramide (hypothetical).

DIBASIC.

$H_2SO_4 + NH_3 - H_2O = NH(SO_2)''\left.\begin{matrix}H\\H\end{matrix}\right\}O$ Sulphamic acid.

$H_2SO_4 + NH_3 - 2H_2O = NH(SO_2)''$ Sulphimide.

$H_2SO_4 + 2NH_3 - H_2O = NH(SO_2)''\left.\begin{matrix}H\\NH_4\end{matrix}\right\}O$ Sulphamate of ammonium.

$H_2SO_4 + 2NH_3 - 2H_2O = N_2H_4(SO_2)''$ Sulphamide.

TRIBASIC.

$H_3PO_4 + NH_3 - H_2O =$ unknown compound.

$H_3PO_4 + NH_3 - 2H_2O = N(PO)'''\left.\begin{matrix}H\\H\end{matrix}\right\}O$ Phosphamic acid.

$H_3PO_4 + NH_3 - 3H_2O = N(PO)'''$ Phosphamide.*

$H_3PO_4 + 2NH_3 - H_2O =$ unknown compound.

$H_3PO_4 + 2NH_3 - 2H_2O = N(PO)'''\left.\begin{matrix}H\\NH_4\end{matrix}\right\}O$ Phosphamate of ammonium.

$H_3PO_4 + 2NH_3 - 3H_2O = N_2H_3(PO)'''$ Phosphodiamide.†

$H_3PO_4 + 3NH_3 - H_2O =$ unknown compound.

$H_3PO_4 + 3NH_3 - 2H_2O = N_2H_3(PO)'''\left.\begin{matrix}H\\NH_4\end{matrix}\right\}O$ Phosphodiamate of ammonium.

$H_3PO_4 + 3NH_3 - 3H_2O = N_3H_6(PO)'''$ Phosphotriamide.

The compound $NH_2(ClO_3)'$ is unknown. Chemists are acquainted, however, with a very great number of compounds formed according to the same typical reaction; for example: —

$$C_2H_4O_2 + NH_3 - H_2O = NH_2(C_2H_3O)' \text{ acetamide.}$$

The amides are all referrible to the types ammonia, diammonia, and triammonia respectively. Monobasic acids yield monamides only, $NH_2(C_2H_3O)'$ for instance. Dibasic acids yield monamides and diamides, $NH(SO_2)''$ and $N_2H_4(SO_2)''$ for instance. Tribasic acids yield monamides, diamides, and triamides, $N(PO)'''$, $N_2H_3(PO)'''$, and $N_3H_6(PO)'''$ for instance. The polybasic acids yield amic acids and amates of ammonium in addition, which bodies are referrible to the compound type of hydrate of ammonia $NH_3\left.\begin{matrix}H\\H\end{matrix}\right\}O$. Very many amides, especially those of monobasic carbon

* Usually called biphosphamide.

† Usually called phosphamide. Sulphamide ought analogically to be called sulphodiamide, and sulphimide sulphamide; but the use of these two words to signify the compounds expressed above is too general to allow of their alteration.

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acids, are susceptible of a further loss of water, whereby they become converted into nitryls. Thus, for instance, acetamide $NH_2(C_2H_3O)'$, — water H_2O, = acetonitryl $N(C_2H_3)'''$, or cyanide of methyl $CH_3.CN$. Amides, amic acids, &c., are not in every case procurable according to the typical reactions figured above. In practice, moreover, they are most of them capable of being produced more advantageously by other processes. The amic acids and their ammonium salts, for instance, are best prepared by the action of ammonia on polybasic anhydrides; and several modes of producing the amides have been already adverted to. But the above equations represent most simply the relations of amides and amic acids, formed no matter how, to their corresponding ammonium salts.

Ammonia has been made to combine with nearly every known acid. The properties of the most important and simple ammoniacal salts of the non-metallic acids are described below, the hydracid salts first, and then in succession the salts of monobasic, bibasic, and tribasic oxygen acids.

Ammoniacal Salts of Hydracids.

(223) Fluoride of Ammonium. *Sym.* NH_4F; *p.n.* 37.—Dry ammoniacal and fluorhydric acid gases combine directly to form this salt. It is best made by subliming a mixture of perfectly dry chloride of ammonium and fluoride of sodium. It occurs in small white prismatic crystals, which are permanent in the air, fusible, and readily volatile. The aqueous solution of the salt has a pungent saline taste, and on evaporation, or by exposure to air, evolves ammonia, whereby it is converted into the fluorhydrate of fluoride of ammonium $NH_4F.HF$. This last compound may be formed as above described; or, by supersaturating silicofluorhydric acid with ammonia, and evaporating to crystallization, after separation of the deposited silica:—

$$H_2SiF_6 + 3NH_3 + 2H_2O = 3(NH_4F.HF) + SiO_2.$$

It forms colourless prismatic crystals, which deliquesce in moist air, and volatilise when heated, giving off white acrid vapours. Its solution etches glass readily.

(224) Chloride of Ammonium. *Sym.* NH_4Cl; *p. n.* 53·5.—This salt, familiarly known as sal-ammoniac, occurs native in volcanic districts, and exists in minute quantity in sea water. Dry ammoniacal and chlorhydric acid gases combine, volume to volume, with considerable evolution of heat, to form an opaque

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white pulverulent deposit of sal-ammoniac, which, when examined microscopically, is seen to be crystallised in forms of the regular system. Sal-ammoniac is made commercially on a very large scale by neutralising gas-liquor or bone-liquor with muriatic acid, evaporating to crystallisation, torrefying the crystals by a gentle heat, and then subliming. Or, the gas liquor may be decomposed by chloride of calcium, the filtered solution of sal-ammoniac crystallised by evaporation, and the crystals dried, torrefied, and sublimed: $(NH_4)_2CO_3 + 2CaCl = Ca_2CO_3 + 2NH_4Cl$. Or, commercial sulphate of ammonium, mixed with common salt, may be submitted at once to sublimation: $(NH_4)_2SO_4 + 2NaCl = Na_2SO_4 + 2NH_4Cl$. Sublimed sal-ammoniac occurs in semi-transparent dome-shaped masses, frequently weighing 5 or 6 cwts. It is extremely tough in structure, and is composed of fibres arranged perpendicularly to the surface of the dome. Sal-ammoniac was at one time obtained almost exclusively from Egypt, where it was made by subliming the soot produced by the combustion of camels' dung. It was afterwards made at Liège by subliming the soot produced by burning a mixture of coal, common salt, animal matter, and clay.

The commercial salt may be purified by dissolving it in water, rendering the liquid slightly alkaline with ammonia, exposing it to the air for some time, filtering, and crystallising by evaporation. Chloride of ammonium usually crystallises in an arborescent form, but well-defined octahedrons can generally be recognised upon the extremities of the spiculæ. It dissolves in about three parts of water at ordinary temperatures, and in about one part at 100°. In the act of dissolving, it produces a great reduction of temperature, whence it is frequently used as an ingredient in frigorific mixtures. Its solution loses ammonia by evaporation or exposure to air, though to a very slight extent only. Sal-ammoniac is scarcely soluble in absolute alcohol. The specific gravity of the salt is 1·5. It is devoid of smell, but has a sharp saline taste. When heated to a temperature below redness, it volatilises unchanged without previous fusion. It combines directly with many more electro-negative chlorides to form double salts, the platino-chloride of ammonium $PtCl_2NH_4Cl$, for example. Its solution even dissolves chloride of silver, with formation of a crystallisable double chloride. When heated with sodium, iron, and some other metals, chloride of ammonium is decomposed with formation of a metallic chloride and liberation of ammonia and hydrogen. When any compounds of metals which form volatile chlorides are heated with excess of chloride of ammonium, decom-

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position ensues, and chlorides of the respective metals are driven off together with sal-ammoniac vapours. Finely powdered and perfectly dry chloride of ammonium, kept cool by ice, absorbs the vapour of sulphuric anhydride to form a translucent mass of chlorosulphite of ammonium, NH_4ClSO_3.

(225) Bromide of Ammonium. *Sym.* NH_4Br; *p. n.* 98.—This salt is made by neutralising solution of ammonia with bromhydric acid, and crystallising by evaporation. It forms arborescent crystals, which volatilise without fusing. It becomes slightly yellow by exposure to air, is freely soluble in water, sparingly soluble in alcohol.

(226) Iodide of Ammonium. *Sym.* NH_4I; *p. n.* 145.—This salt is most readily made by decomposing a solution of iodide of iron with carbonate of ammonium, filtering, and evaporating. It occurs in white ill-defined cubical crystals. Out of access of air, it volatilises unchanged, but the sublimate produced in presence of air contains free iodine. Iodide of ammonium is very deliquescent, and readily soluble both in water and alcohol. Its aqueous solution becomes yellow by exposure to air.

(227) Cyanide of Ammonium. *Sym.* NH_4CN; *p.n.* 44.—This compound is produced by the direct combination of equal volumes of ammoniacal and cyanhydric acid gases. It is best made by distilling from a water-bath a mixture of sal-ammoniac with some metallic cyanide, usually the double cyanide of potassium and iron (yellow prussiate of potash). The product may be condensed in a tube surrounded by a freezing mixture. Cyanide of ammonium also results from passing dry ammonia over ignited charcoal, as previously referred to; and from passing a mixture of carbonic oxide and ammoniacal gases through a red-hot tube: $CO + 2NH_3 = NH_4CN + H_2O$. The salt crystallises in cubes, or in stauroid tufts. It is readily soluble in water and alcohol, has a strong penetrating odour, and is a most violent poison. It boils at 36°, producing a vapour, which burns with a yellowish flame, evolving fumes of carbonate of ammonium. It is a very unstable salt, and, even at ordinary temperatures, is gradually converted into an ill-defined brown substance, known as azulmic acid. It is rapidly attacked by chlorine, with formation, among other products, of gaseous chloride of cyanogen.

(228) Hydrate of Ammonium. *Sym.* NH_4HO; *p.n.* 35.—The solution of ammoniacal gas in water resembles, in very many of its reactions, the hydrate of an alkali-metal. The composition of the crystals which concentrated aqueous ammonia yields at −40° has not been ascertained, but they probably constitute a definite

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hydrate. The hydrates of certain derivatives of ammonia, moreover, are well known in the isolated state. The hydrate of tetrethylium $N(C_2H_5)_4HO$, for instance, occurs as a deliquescent, non-volatile, crystalline solid, of a caustic taste and soapy feel, which rapidly absorbs carbonic anhydride from the atmosphere, corresponding in all these particulars to hydrate of sodium NaHO. Solution of ammonia usually decomposes metallic salts in a manner closely resembling that of hydrate of sodium or potassium, as illustrated in the following varieties of reactions. By adding hydrate of sodium or ammonium to an excess of sulphate of copper, for instance, we precipitate the same basic sulphate of the metal. By adding an excess of either hydrate to perchloride of iron we precipitate the same hydrated sesquioxide of iron. Again, by adding an excess of either hydrate to chloride of zinc, we precipitate and redissolve hydrate of zinc with formation of analogous sodium and ammonium double oxides. And lastly, by adding an excess of either hydrate to uranic nitrate, we precipitate a corresponding uranite of sodium or ammonium, NaU_2O_4 and $NH_4U_2O_4$ respectively.

In some cases, however, the solution of ammonia reacts in a manner altogether different from that of the fixed alkalies. Thus, when hydrate of sodium is added to solution of chloride of mercury, we obtain a yellow precipitate of hydrate of mercury: —

$$HgCl + NaHO = NaCl + HgHO.$$

But when solution of ammonia is added to chloride of mercury, we obtain a white precipitate of chloride of dimercurammonium, and similarly in other instances: —

$$2HgCl + 2NH_3 = NH_4Cl + NH_2Hg_2Cl.$$

Moreover, although the hydrates of sodium and ammonium alike precipitate and redissolve certain metallic hydrates, it is not clear that the soluble products so formed are, in all cases, of analogous composition. Some of the ammonium compounds appear to belong to the class of ammoniated salts, which will be subsequently described. Neither oxide of ammonium $(NH_4)_2O$, nor any well-defined derivative thereof by the mere displacement of hydrogen, is known to chemists.

(229) Sulphydrate of Ammonium. *Sym.* NH_4HS; *p. n.* 51.— Dry ammoniacal and sulphydric gases combine with one another, volume to volume, to form this compound. It occurs in almost colourless crystalline plates, which volatilise without decomposition, even at ordinary temperatures. The solution of the salt is made

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by passing sulphydric acid gas into aqueous ammonia. The liquid is primarily colourless, but, by the action of air, it becomes yellow from the liberation of sulphur, which at first remains in solution. By continued exposure, thiosulphate, sulphite, and sulphate of ammonium are successively formed, with deposition of sulphur, and re-production of a colourless liquid. Sulphydrate of ammonium solution dissolves electronegative sulphides, with formation of sulphur-salts, and most frequently with liberation of sulphydric acid, thus: —

$$2NH_4HS + SnS_2 = (NH_4)_2SnS_3 + H_2S.$$

When added to salts, the metals of which form sulphides but not sulphydrates, it is also decomposed, with liberation of sulphydric acid gas, thus: —

$$2NH_4HS + 2PbCl = 2NH_4Cl + Pb_2S + H_2S.$$

A bichloro-derivative of sulphydrate of ammonium $(NH_3Cl)ClS$, results from the action of dry ammonia upon an excess of protosulphide of chlorine.

(230) SULPHIDE OF AMMONIUM. *Sym.* $(NH_4)_2S$; *p. n.* 68.—At the temperature of −18°, two volumes of sulphydric acid combine with four volumes of ammonia to form this compound. Or, it may be made by subliming a mixture of sulphide of potassium with chloride of ammonium, and condensing the product at −18°. It forms colourless crystals, having a marked alkaline reaction. At ordinary temperatures, it is decomposed into sulphydrate of ammonium and free ammonia. It dissolves readily in water, undergoing, in all probability, a similar decomposition. This solution is generally made by taking two equal portions of aqueous ammonia, saturating one with sulphydric acid, and then adding the other to it. Like the solution of the sulphydrate, this liquid is at first colourless, then, by exposure to air, yellow, and finally colourless, with deposition of sulphur. A chloro-derivative of sulphide of ammonium $(NH_3Cl)_2S$, results from the action of an excess of dry ammonia upon protosulphide of chlorine.

(231) BISULPHIDE OF AMMONIUM. *Sym.* $(NH_4)_2S_2$; *p. n.* 100.—This salt may be obtained in transparent, yellow, deliquescent crystals, by passing ammoniacal gas and sulphur vapour through a red-hot porcelain tube. It constitutes the first product of the action of air upon solution of sulphydrate of ammonium: —

$$4NH_4HS + O_5 = (NH_4)_2S_2 + (NH_4)_2S_2O_3 + 2H_2O.$$

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It also forms the principal ingredient of *Boyle's fuming liquor*, which is distilled from a mixture of sal-ammoniac, sulphur, and quicklime; or from a mixture of sal-ammoniac, sulphur, and a sulphide of calcium procured by heating sulphur with slaked lime. It condenses as a yellow, oily, fœtid liquid, which fumes strongly in the air, and sometimes deposits yellow lamellar crystals of the bisulphide. It dissolves sulphur to form a non-fuming syrupy liquid. Its aqueous solution also dissolves sulphur in large quantity to form a pentasulphide of ammonium, which may be crystallised therefrom in orange-yellow oblique rhombic prisms. By the spontaneous decomposition of this pentasulphide, ruby-red crystals of a heptasulphide, to which there is no corresponding potassium compound, are produced: —

$$3(NH_4)_2S_5 = 2(NH_4)_2S_7 + NH_4HS + NH_3.$$

A chloro-derivative of bisulphide of ammonium $(NH_3Cl)_2S_2$, is formed by the combination of dry ammonia with bisulphide of chlorine.

(232) Selenhydrate of Ammonium. *Sym.* NH_4HSe; *p.n.* 98·5. Ammoniacal and selenhydric gases condense in equal volumes to form a white crystalline mass, which is quickly decomposed by the action of air with separation of selenium. Its solution in water undergoes a still more speedy decomposition. A selenide of ammonium $(NH_4)_2Se$ has also been described. The tellurhydrate and telluride of ammonium resemble the corresponding selenium compounds.

(233) Amides of Ammonium.—The ammoniacal salts hitherto described may be looked upon as pertaining to mixed amide-chloride and amide-oxide types, thus: —

$$\overbrace{H_3N.HF, \quad H_3N.HCl.}^{\text{Amide-chloride.}} \qquad \overbrace{H_3N.H_2O, \quad H_3N.H_2S.}^{\text{Amide-oxide.}}$$

Now, by having regard to derived ammonias, we are able also to adduce illustrations of compounds pertaining to the amide-amide type, although indeed such bodies can scarcely be considered as salts: —

$$\overbrace{H_3N.H_3N, \quad H_3N.H_3P.}^{\text{Amide-amide.}}$$

Thus, we have carbodiamide $(CO)''HN.H_3N$, sulphodiamide $(SO_2)''HN.H_3N$, ethylendiamine $(C_2H_4)''HN.H_3N$, phenylendiamine $(C_6H_4)''HN.H_3N$, &c. Or, we might express the relations of these bodies to ammoniacal salts on the ammonium theory, whereby we

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should have molecules of chlorhydric acid, water, and ammonia, in each of which one atom of hydrogen was displaced by one atom of ammonium, thus: —

$$H_4N.Cl, \qquad H_4N.HO, \qquad (CO)''H_2N.H_2N.$$

But these bodies are usually represented by the less assumptive formulæ—

$(CO)''H_4N_2$, $(SO_2)''H_4N_2$, $(C_2H_4)''H_4N_2$, and $(C_6H_4)''H_4N_2$

respectively. It seems, indeed, that two atoms of hydrogen, each belonging to a different molecule of ammonia $\begin{Bmatrix} H_3N \\ H_3N \end{Bmatrix}$, are displaced by one atom of a di-equivalent radicle, thus $(CO)''^{H_2N}_{H_2N}$; and that this displacement of two separable atoms by one inseparable atom, binds the two simple amides into one complex diamide molecule. It must be remembered, however, that succindiamide $(C_4H_4O_2)''H_4N_2$, for instance, breaks up into succinimide $(C_4H_4O_2)''HN$, and ammonia H_3N; and that, on the other hand, carbimide $(CO)''HN$, for instance, unites directly with ammonia H_3N, to form carbodiamide $(CO)''H_4N_2$, although indeed these decompositions and combinations may be explained in a different way.* Hofmann has succeeded, by a very beautiful reaction, somewhat resembling that just described, in obtaining mixed amine-phosphine $H_3N.H_3P$, and phosphine-arsine $H_3P.H_3As$, compounds, &c. Bromide of bromethyl-triethyl-phosphonium $(C_2H_4Br)Et_3PBr$, for instance, unites with triethylamine Et_3N, to form the bibromide of ethylen-hexethyl-phosphine-ammonium, corresponding to the free base $(C_2H_4)''Et_4NP$, or $(C_2H_4)''EtP.Et_3N$.

Ammoniacal Salts of Monobasic Oxacids.

(234) Chlorate of Ammonium. *Sym.* NH_4ClO_3; *p. n.* 101·5. —The hypochlorite of ammonium NH_4ClO, appears to have no existence. Even a very dilute solution of hypochlorous acid, rendered neutral or alkaline with ammonia, evolves bubbles of nitrogen continuously until it is completely decomposed. Aqueous chlorite of ammonium NH_4ClO_2, made by neutralising solution of chlorous acid with ammonia, is slightly more stable than the hypochlorite solution, but does not admit of concentration. Chlorate of ammonium NH_4ClO_3, may be obtained by precipitating a solution of chlorate of barium with carbonate of ammonium, and evapo-

* Succinimide $(C_4H_4O_2)''HN$, ought possibly to be represented as disuccindiamide $(C_4H_4O_2)''_2H_2N_2$, carbimide as dicarbodiamide $(CO)''_2H_2N_2$, &c.

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rating the filtered liquid in a water-bath; or, by neutralising aqueous chloric acid with ammonia and evaporating. The salt crystallises in fine needles, which are very soluble both in water and alcohol. These crystals explode with a red light when placed on a hot surface, and sometimes even spontaneously. Bromate of ammonium NH_4BrO_3, is made by the same process, and in every respect resembles the chlorate, save that it is somewhat less stable. Iodate of ammonium NH_4IO_3, is made by neutralising a solution of iodic acid or terchloride of iodine with ammonia, whereby the salt is deposited as a sparingly soluble crystalline precipitate. It may also be obtained in brilliant colourless cubes by slow evaporation. At about 150° it is decomposed, with evolution of equal volumes of oxygen, nitrogen, and iodine gases: —

$$NH_4IO_3 = 2H_2O + I + N + O.$$

(235) PERCHLORATE OF AMMONIUM. *Sym.* NH_4ClO_4; *p. n.* 117·5.—This salt may be made by neutralising perchloric acid with ammonia, or by decomposing perchlorate of barium with carbonate of ammonium. It forms colourless transparent needles belonging to the right prismatic system. It is soluble in five parts of cold water, and sparingly soluble in alcohol. Its aqueous solution is neutral, but becomes acid by evaporation. It explodes when heated, though much less readily than the chlorate. The periodate of ammonium NH_4IO_4, closely resembles the perchlorate.

(236) NITRITE OF AMMONIUM. *Sym.* NH_4NO_2; *p. n.* 64.—This compound is procurable by decomposing solution of nitrite of silver with chloride, or solution of nitrite of lead with sulphate of ammonium. The filtrate may be evaporated, in vacuo, over oil of vitriol. The salt occurs as an imperfectly crystallised saline mass. Its aqueous solution is decomposed, when gently heated, into nitrogen gas and water: $NH_4NO_2 - 2H_2O = N_2$. The decomposition is gradual when the solution has an alkaline, sudden when it has an acid reaction.

(237) NITRATE OF AMMONIUM. *Sym.* NH_4NO_3; *p.n.* 80.—Diluted nitric acid is neutralised with carbonate of ammonium, and the liquid evaporated to the crystallising point. The salt occurs in long flexible needles, or, if the crystallisation has been very slowly effected, in six-sided prisms. It is also deposited as a dense fibrous mass from a highly concentrated solution. Its sp. gr. is 1·7; its taste bitter and unpleasant. It deliquesces somewhat by exposure to air, and is said to acquire a slight acid reaction. It dissolves in little more than half its weight of cold water, and by

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its solution produces a great reduction of temperature, whence it is frequently employed as an ingredient in frigorific mixtures. The dry salt fuses at 108°, and volatilises unchanged at 180°. It is decomposed freely at 250° into water and nitrous oxide; but at a much higher temperature yields nitrogen, nitric oxide, and ammoniacal gases in addition: $NH_4NO_3 - 2H_2O = N_2O$. Heated with chloride of ammonium, a mixture of nitrogen and chlorine gases is evolved: $2NH_4NO_3 + NH_4Cl = N_5 + Cl + 6H_2O$. Fused nitrate of ammonium acts more or less decidedly upon most of the metals. A piece of zinc dipped into the melted salt disappears rapidly with an effervescence of nitrogen, and considerable development of heat. The fused mixture of nitrate and chloride of ammonium, especially if a little fixed alkaline nitrate be also present, reacts still more violently, and is capable of dissolving not only gold but also the platinum metals.

(238) FORMATE OF AMMONIUM. *Sym.* $CH(NH_4)O_2$*; *p. n.* 63.—This salt is obtained by neutralising formic acid with ammonia or carbonate of ammonium. It crystallises in right rectangular prisms terminated by four-sided pyramids. It is very deliquescent, and soluble both in water and alcohol. It melts at 120°; gives off a little ammonia at a somewhat higher temperature; and, when briskly heated to about 200°, is decomposed entirely into water and cyanhydric acid: $CH(NH_4)O_2 - 2H_2O = H(CN)$. Formamide is unknown; it should result from the reaction: $CH(NH_4)O_2 - H_2O = NH_2(CHO)$. Thioformic acid unites with ammonia to form thioformate of ammonium $CH(NH_4)OS$.

(239.) ACETATE OF AMMONIUM.—*Sym.* $C_2H_3(NH_4)O_2$†; *p. n.* 77.—This is a white inodorous salt, made by saturating glacial acetic acid with dry ammonia. When gently heated, it is partly volatilised, partly decomposed into water and acetamide: $C_2H_3(NH_4)O_2 - H_2O = NH_2(C_2H_3O)$. When heated with phosphoric anhydride, it loses another atom of water to form acetonitryl, or cyanide of methyl, precisely as formate of ammonium yields cyanide of hydrogen: $C_2H_3(NH_4)O_2 - 2H_2O = CH_3(CN)$. Acetate of ammonium is deliquescent, and very soluble both in water and alcohol. Its aqueous solution is made by neutralising dilute acetic acid with carbonate of ammonium. This solution gives off ammonia by evaporation, and yields an acid salt crystallising in fine radiating needles. The acid salt, $C_2H_3(NH_4)O_2 . C_2H_4O_2$, may also be obtained as a white sublimate by heating a mixture of equal parts of sal-ammoniac and acetate of potassium, one half the ammonia

* Formic acid, CH_2O_2. † Acetic acid, $C_2H_4O_2$.

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being evolved in the free state. Various halogen derivatives of acetate of ammonium, made by neutralising with ammonia the halogen derivatives of acetic acid, have been described. Of these, the best known is the trichloracetate of ammonium $C_2Cl_3(NH_4)O_2.2H_2O$. This salt crystallises in prisms which melt at 80°, and are very soluble in water. When heated with phosphoric anhydride, it yields trichloracetonitryl, or cyanide of trichloromethyl $CCl_3(CN)$. Thiacetic acid unites with ammonia to form thiacetate of ammonium $C_2H_3(NH_4)OS$. The propionate of ammonium $C_3H_5(NH_4)O_2$, and the acrylate $C_3H_3(NH_4)O_2$, correspond closely in their properties and modes of formation to the acetate.

(240) CYANATE OF AMMONIUM. *Sym.* NH_4CNO; *p. n.* 60.— When vapours of cyanic acid are led into dry ammoniacal gas, a white voluminous crystalline body condenses, which constitutes this salt. It is very soluble in water, forming a solution which evolves cyanic acid when treated with acids, and ammonia when treated with alkalies. The same solution may be made by decomposing cyanate of silver with aqueous sal-ammoniac. When cyanate of ammonium is gently heated, or when its solution is either boiled or left to itself for some days, the salt undergoes a peculiar isomeric transmutation, and is converted into urea or carbamide $N_2H_4(CO)''$, a crystalline organic base, having none of the characters of cyanic or ammoniacal salts.

(241) SULPHOCYANATE of AMMONIUM. *Sym.* NH_4CNS; *p.n.* 76. This salt may be prepared by decomposing sulphocyanate of copper with aqueous sulphydrate of ammonium, and evaporating the filtrate. Or, by heating aqueous cyanhydric acid with ammonia and sulphur, dissolved in sulphydrate of ammonium: $HCN + NH_3 + S = NH_4CNS$. Sulphocyanate of ammonium is very soluble, both in water and alcohol. It is most easily crystallised from alcohol, but may also be obtained in white anhydrous deliquescent crystals by allowing its concentrated aqueous solution to evaporate spontaneously over oil of vitriol. The salt fuses at 145° into a colourless liquid, which at about 200° is decomposed into bisulphide of carbon, sulphydrate of ammonium, and melam: —

$$4NH_4CNS = CS_2 + 2NH_4HS + C_3H_6N_6.$$

AMMONIACAL SALTS OF BIBASIC OXACIDS.

(242) ACID SULPHITE OF AMMONIUM. *Sym.* NH_4HSO_3; *p.n.* 99.— This salt is formed by saturating aqueous ammonia with sulphurous

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acid, or by subliming neutral sulphite of ammonium, which thereby breaks up into acid sulphite and free ammonia. A similar acid selenite of ammonium, NH_4HSeO_3, has also been obtained in crystalline needles, permanent in the air.

(243) SULPHITE OF AMMONIUM. *Sym.* $(NH_4)_2SO_3$; *p.n.* 116.—When sulphurous acid or anhydride is passed through excess of aqueous ammonia, combination takes place, attended with a considerable elevation of temperature. The salt crystallises out, on cooling, in colourless six-sided prisms, terminated by six-sided pyramids. By exposure to air, it changes gradually into sulphate of ammonium. It dissolves in less than its own weight of cold water, forming a solution which evolves ammonia freely on boiling. The salt, when heated, loses ammonia, and yields a sublimate consisting principally of the acid sulphite, but also containing some thionamate of ammonium, or possibly thionamide. A corresponding selenite of ammonium $(NH_4)_2SeO_3$, crystallised in four-sided prisms, has been described.

(244) ACID SULPHATE OF AMMONIUM. *Sym.* NH_4HSO_4; *p.n.* 115.—This salt is formed by adding one part of dilute sulphuric acid to another part previously neutralised with carbonate of ammonium. It crystallises in thin rhombohedrons, or in scales. It is deliquescent and soluble in its own weight of cold water.

(245) SULPHATE OF AMMONIUM. *Sym.* $(NH_4)_2SO_4$; *p.n.* 132.—This salt is made commercially on a very large scale, from gas liquor, which consists principally of an impure solution of carbonate and sulphydrate of ammonium. The distilled liquor is neutralised with sulphuric acid and evaporated to crystallisation, or, in some cases, it is merely filtered through beds of gypsum, and then evaporated. The resulting crude salt is used principally for agricultural purposes, and for the manufacture of sal-ammoniac and ammonium-alum. Crude sulphate of ammonium is sometimes purified by fusion and recrystallisation from water; but for laboratory purposes, the salt is usually made by neutralising dilute sulphuric acid with carbonate of ammonium, and crystallising by evaporation. It occurs in colourless transparent crystals, belonging to the right prismatic system, and isomorphous with those of sulphate of potassium. Its sp. gr. is 1·75. It becomes slightly moist on exposure to air, is soluble in twice its weight of cold, and in an equal weight of boiling water. When first heated, it decrepitates; at 140° it melts; and at a much higher temperature decomposes. The products of its decomposition by heat have not been accurately examined. It seems, however, to produce acid sulphate, acid sulphite, and sulphamate of ammonium, together with some sulphamide. Thio-

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sulphate of ammonium $(NH_4)_2S_2O_3$, is a deliquescent and very soluble salt, crystallising in rhombic laminæ.

(246) Acid Carbonate of Ammonium. *Sym.* NH_4HCO_3; *p.n.* 79. — This is the most permanent carbonate of ammonium, into which all others become finally converted by exposure to air. It has been found native in large well-defined crystals among altered deposits of Patagonian guano. It may be prepared by exposing commercial sesquicarbonate of ammonium to the air; or by treating it with cold water, or, preferably, with alcohol, whereby normal carbonate of ammonium is dissolved away, and the acid carbonate left almost unacted upon. Or, a solution of the commercial carbonate may be saturated with carbonic acid or anhydride. It may be obtained in large crystals, belonging to the right prismatic system, by pouring boiling water on to the powdered sesquicarbonate, and allowing the solution to cool in a tightly corked flask. Acid carbonate of ammonium volatilises slowly at ordinary temperatures. Its sp. gr. is 1·59. It dissolves in eight parts of cold water, forming a solution which gives off carbonic acid slowly at ordinary temperatures, rapidly at 36° and upwards. When treated with warm spirit, it also evolves carbonic acid, and produces a solution of normal carbonate.

(247) Carbonate of Ammonium. *Sym.* $(NH_4)_2CO^3$; *p.n.* 96.— This compound cannot be isolated, and is known only in solution. When sesquicarbonate of ammonium is dissolved in alcohol and saturated with ammonia, the salt which deposits is still the sesquicarbonate. A medicinal preparation of normal carbonate of ammonium is made by distilling a mixture of sal-ammoniac and carbonate of potassium with rectified spirit, or by dissolving the commercial sesquicarbonate in rectified spirit at a gentle heat, whereby the excess of carbonic acid is evolved. Aqueous solutions may be obtained by the same processes, or by the careful addition of ammonia to solution of the sesquicarbonate. When normal carbonate of ammonium is decomposed by chloride of barium, the filtered liquid should be free from any hydrate of barium, which would indicate the presence of an excess of ammonia; and also from any acid carbonate of barium, which would indicate an excess of carbonic acid. Normal carbonate of ammonium is the principal constituent of gas-liquor, and of the product distilled from bones, &c.

(248) Sesquicarbonate of Ammonium. *Sym.* $H_2(NH_4)_4(CO_3)_3$, or $2NH_4HCO_3 . (NH_4)_2CO_3$; *p. n.* 254. — The crystallised salt may be obtained by dissolving the commercial sesquicarbonate in strong aqueous ammonia, and then adding a little

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alcohol. It is deposited in very fine, perfectly transparent, right rectangular prisms, containing two atoms of water of crystallization. These crystals, when acted upon by cold water or alcohol, break up into normal carbonate which dissolves, and acid carbonate which remains crystallized in its own proper form. The salt is also completely converted into acid-carbonate by exposure to air.

The composition of commercial sesquicarbonate of ammonium is represented by the formula $2NH_4HCO_3 . (NH_3)_2CO_3$, or the constituent normal carbonate of the pure salt has lost an atom of water, to become converted into carbamate of ammonium $\left.\begin{matrix}NH_2(CO)''\\NH_4\end{matrix}\right\}O$. It was formerly made by directly subliming the products of the dry distillation of bones and other animal matter, but is now always obtained by heating a mixture of chalk and sal-ammoniac in iron retorts. The sublimate is condensed in large leaden chambers, and is usually purified by resublimation at a lower temperature:—

$$6NH_4Cl + 3Ca_2CO_3 = 2NH_4HCO_3.(NH_2)_2CO_2 + H_2O + 2NH_3 + 6CaCl.$$

It occurs in white, fibrous, translucent cakes, about two inches thick, having a strongly ammoniacal taste and smell. It evolves ammonia by exposure to air, being thereby converted into an opaque pulverulent mass of acid-carbonate. Cold water or alcohol dissolves out the carbamate of ammonium, and leaves a residue of acid-carbonate. Boiling water or alcohol decomposes it more or less completely into neutral carbonate, which is dissolved, and carbonic acid, which is driven off. Commercial sesquicarbonate of ammonium is occasionally contaminated with traces of lead, calcium, empyreumatic oil, and sulphate, thiosulphate, and chloride of ammonium, but it is for the most part extremely pure. Several other carbonates of ammonium have been described by Rose.

Combinations of ammonia with the homologues of carbonic acid have been obtained, the acid glycolate $C_2(NH_4)H_3O_3$, and acid lactate $C_3(NH_4)H_5O_3$, for example. The last named salt occurs in deliquescent prismatic crystals.

(249) SULPHOCARBONATE OF AMMONIUM. *Sym.* $(NH_4)_2CS_3$; *p. n.* 144.—This salt is made by adding one volume of bisulphide of carbon to ten volumes of alcohol saturated with ammonia. As soon as the mixture has assumed a brownish yellow colour, it is placed in ice-water, and after standing for an hour, the mother-liquor is poured off from the deposited crystals, which are washed with alcohol and then with ether, dried between folds of bibulous

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paper, and preserved in a well-stoppered bottle. It is a pale yellow crystalline salt, which volatilises even at ordinary temperatures. It is deliquescent, and very soluble in water. Its solution is decomposed by exposure to air, with formation of dark-brown coloured products, as are also the crystals when moistened with water or alcohol.

(250) ACID OXALATE OF AMMONIUM. *Sym.* $NH_4HC_2O_4$; *p. n.* 107.—This salt is obtained by adding oxalic acid, or even sulphuric, chlorhydric or nitric acid, to a solution of the neutral salt, than which it is much less soluble. It crystallises with one atom of water in forms belonging to the right prismatic system. Its solution has a strongly acid reaction. Its sp. gr. is 1·61. It is decomposed by heat into water, oxamic acid, and other products.

(251) OXALATE OF AMMONIUM. *Sym.* $(NH_4)_2C_2O_4$; *p. n.* 124.—This salt has been found native in guano. It is made by neutralising a solution of oxalic acid with carbonate of ammonium, and crystallizing by evaporation. It occurs in colourless, prismatic, tufted prisms, belonging to the right prismatic system. The crystallized salt is soluble in three parts of cold water. Its sp. gr. is 1·5. It contains one atom of water of crystallization, which it loses by efflorescence in warm air. It is decomposed by heat, partly into water and oxamide, partly into other products, including carbonate of ammonium and carbonic oxide:—

$$(NH_4)_2C_2O_4 - 2H_2O = N_2H_4(C_2O_2)''.$$

(252) QUADROXALATE OF AMMONIUM. *Sym.* $NH_4H_3(C_2O_4)_2$, or $NH_4HC_2O_4.H_2C_2O_4$; *p. n.* 197.—When a solution of equal proportions of oxalic acid and acid oxalate of ammonium is evaporated, this salt crystallises out on cooling. The crystals, which contain two atoms of crystallization-water, occur in forms of the doubly oblique system, and are isomorphous with those of quadroxalate of potassium. The sp. gr. of the salt is 1·65. It loses its water of crystallization at 100°. It is very soluble in hot water.

(253) ACID STANNATE OF AMMONIUM. *Sym.* NH_4HSnO_3; *p. n.* 185. — Recently precipitated stannic acid dissolves in aqueous ammonia. The solution, evaporated over oil of vitriol, leaves a jelly-like residue, having the above composition. Sulphostannate of ammonium $(NH_4)_2SnS_3$ is made by dissolving stannic sulphide in sulphydrate, or stannic acid in polysulphide of ammonium. A silicate of ammonium, probably $(NH_4)_2SiO_3$, may be obtained by dissolving freshly precipitated silica in aqueous ammonia.

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Ammoniacal Salts of Tribasic Oxacids.

(254) Phosphite of Ammonium. *Sym.* $(NH_4)_2HPO_3$; *p. n.* 116.—The hypophosphite of ammonium $NH_4H_2PO_2$, has not been minutely examined. The phosphite is made by saturating aqueous phosphorous acid with ammonia, and crystallising by evaporation. It occurs in large four-sided prisms, with quadrilateral summits, which are very deliquescent. It is resolved by heat into ammonia, water, phosphuretted hydrogen, and metaphosphoric acid.

(255) Bi-acid Phosphate of Ammonium. *Sym.* $NH_4H_2PO_4$; *p. n.* 115.—When phosphoric acid is added to common monacid phosphate of ammonium, or to ammonia, until a strongly acid solution is formed which gives no precipitate with chloride of barium, this salt is produced, and may be obtained by evaporation. It crystallises in the square prismatic system. When heated, it gives off water and ammonia, leaving metaphosphoric acid. It is somewhat less soluble in water than the monacid phosphate.

(256) Monacid Phosphate of Ammonium. *Sym.* $(NH_4)_2HPO_4$; *p. n.* 132.—This salt is made commercially by precipitating a solution of bi-acid phosphate of calcium (bone-earth dissolved in sulphuric or chlorhydric acid) with a slight excess of carbonate of ammonium, filtering and evaporating. It may be purified by re-solution and crystallisation. It forms large, colourless, transparent crystals, belonging to the oblique prismatic system. It has a cooling saline taste, and marked alkaline reaction. It effloresces slightly by exposure to air, giving off ammonia. It dissolves in four parts of cold, and in a smaller quantity of hot water. Its dilute solution, when boiled, becomes converted into that of the bi-acid phosphate. At a red heat, it is completely decomposed, leaving a residue of metaphosphoric acid: $(NH_4)_2HPO_4-(2NH_3+H_2O)=HPO_3$.

(257) Phosphate of Ammonium. *Sym.* $(NH_4)_3PO_4$; *p. n.* 149.—This salt separates as a crystalline magma when strong aqueous ammonia is added to a solution of the monacid phosphate. On drying, it loses ammonia, to re-form the monacid-phosphate.

(258) Arsenites of Ammonium.—There appear to be two arsenites, $NH_4H_2AsO_3$ and $(NH_4)_2HAsO_3$ respectively, but neither of them is well defined. The former salt occurs as a viscid crystalline deposit, when aqueous ammonia is poured upon pulverised arsenious anhydride. According to Pasteur, the crystals are oblique rectangular prisms, simulating hexagonal tables through the displacement of two of their edges by planes. By an excess of water, or by exposure to air, both salts are converted into arsen-

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ious anhydride, water, and ammonia. Monacid sulpharsenite of ammonium $(NH_4)_2HAsS_3$, is made by dissolving orpiment in sulphydrate of ammonium. Alcohol precipitates from the solution white feathery crystals of the normal salt $(NH_4)_3AsS_3$, which are decomposed on exposure to air.

(259) Bi-acid Arsenate of Ammonium. *Sym.* $NH_4H_2AsO_4$; *p. n.* 159.—This salt is made by supersaturating ammonia with solution of arsenic acid and evaporating. It forms large crystals, isomorphous with those of the bi-acid phosphate. It is deliquescent, very soluble in water, and has a strongly acid reaction. A corresponding sulpharsenate $NH_4H_2AsS_4$, soluble in alcohol, has been obtained. The antimonate of ammonium, which deposits on cooling a solution of antimonic acid in warm aqueous ammonia, seems to correspond to the formula, $NH_4H_2SbO_4 . H_2O$.

(260) Monacid-arsenate of Ammonium. *Sym.* $(NH_4)_2HAsO_4$; *p. n.* 176.—By adding ammonia to a concentrated aqueous solution of arsenic acid till a precipitate is produced, and warming the liquid until the precipitate is redissolved, this salt is formed, and, on cooling, is deposited in beautiful crystals, isomorphous with those of monacid phosphate of ammonium. It has an alkaline reaction, and is slightly efflorescent. The corresponding sulpharsenate $(NH_4)_2HAsS_4$, has been made by dissolving pentasulphide of arsenic in sulphydrate of ammonium.

(261) Arsenate of Ammonium. *Sym.* $(NH_4)_3AsO_4$; *p. n.* 193.—When ammonia is added to a solution of the monacid arsenate, this salt is deposited as a crystalline magma, which evolves ammonia by exposure to air. The corresponding sulpharsenate $(NH_4)_3AsS_4$, is made by dissolving pentasulphide of arsenic in excess of sulphydrate of ammonium, at a gentle heat, and then adding alcohol. On cooling, the tribasic sulpharsenate separates in colourless prisms, which are tolerably permanent; while the bi-acid salt remains in solution. A corresponding sulphantimonate of ammonium $(NH_4)_3SbS_4$, has been obtained by digesting tersulphide of antimony in yellow sulphide of ammonium, and precipitating with alcohol.

(262) Bi-acid Cyanurate of Ammonium. *Sym.* $NH_4H_2(CN)_3O_3$; *p.n.* 146.—This salt is formed by adding ammonia to a warm aqueous solution of cyanuric acid. On cooling, it is deposited in very brilliant white prisms, which contain one atom of water of crystallisation, and effloresce by exposure to air. Cyanurate of ammonium also sublimes in tufts of needles during the dry distillation of uric acid. The neutral and monacid salts are unknown.

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(263) BIBORATE OF AMMONIUM. *Sym.* $(NH_4)H_5B_2O_6$; *p.n.* 141.—Several borates of ammonium have been described, of which this salt, corresponding to octahedral borax, and the quadriborate are the best defined. The biborate is made by dissolving a considerable quantity of boric acid in warm aqueous ammonia. On cooling, it crystallises out in semi-transparent acute rhombic octahedrons, with truncated edges and angles. It is soluble in twelve parts of cold water, and has a marked alkaline reaction. It effloresces in the air, giving off water and ammonia to form the quadriborate $(NH_4)H_5B_4O_9$. This last salt may be prepared directly by saturating warm aqueous ammonia with boric acid, and slowly cooling. It crystallises in transparent six-sided prisms, belonging to the right prismatic system. It is soluble in eight parts of cold water. Its solution has a bitter hot taste, and an alkaline reaction. When boiled, it evolves ammonia. The crystals are permanent in the air, and on ignition, leave vitrified boric anhydride.

AMMONIATED SALTS.

(264) A very great number of metallic salts, chlorides, nitrates, sulphates, &c., are capable of absorbing ammonia in one or more atomic proportions. Confining our attention to the case of metallic protochlorides, we are able to obtain compounds referrible to the following general formulæ: $MCl.NH_3$, the ammoniated chlorides of zinc, cuprosum, cupricum, mercurosum, and platinosum, for example; $MCl.2NH_3$, the ammoniated chlorides of zinc, cobalt, cupricum, silver, and platinosum, for example; $MCl.3NH_3$, the ammoniated chlorides of cadmium, nickel, and cupricum, for example; and $MCl.4NH_3$, the ammoniated chlorides of calcium and strontium, for example. Several of the ammoniated chlorides, produced at a high temperature, correspond to the formula $2MCl.NH_3$, those of zinc and mercuricum, for instance; whilst ammoniated chloride of silver has been sometimes referred to the type $2MCl.3NH_3$. The above ammoniated compounds have been regarded by several chemists as salts of ammonium in which, according to a by no means improbable assumption, there has been a displacement of one or more of the hydrogen-atoms, by one or more atoms of ammonium, thus:—

$$MCl + NH_3 = N\{H_3M\}Cl$$
$$MCl + 2NH_3 = N\{(NH_4)H_2M\}Cl$$
$$MCl + 3NH_3 = N\{(NH_4)_2HM\}Cl$$
$$MCl + 4NH_3 = N\{(NH_4)_3M\}Cl$$

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Several of these ammoniated chlorides have the property of combining with simple metallic chlorides to form double salts. Among these double compounds might be included the ammoniated chloride of mercury formed at a high temperature, $N\{H_3Hg\}Cl.HgCl$, and sesqui-ammoniated chloride of silver, $N\{(NH_4)_2HAg\}Cl.AgCl$.

By the action of ammonia upon chlorides and other salts, we also obtain ammoniated compounds, in which more than one atom of hydrogen is displaced by metal. Thus we have fusible white precipitate NH_3HgCl, infusible white precipitate NH_2Hg_2Cl, and hydrated chloride of tetramercurammonium $NHg_4Cl.H_2O$: and similarly in other instances. The different ammoniated chlorides are usually made by the action of ammonia upon the dry chlorides or their aqueous solutions; and the resulting compounds often differ much in appearance from their corresponding metallic chlorides. Thus mercurous chloride Hg_2Cl, is white, and the ammoniated compound NH_3Hg_2Cl, black; while chloride of platinosum $PtCl$, has scarcely any resemblance to the green salt of Magnus NH_3PtCl, &c. Many ammoniated salts are soluble in water, and crystallisable; that of zinc NH_3ZnCl, and that of mercury NH_3HgCl, for instance. By the action of a gradually increasing heat most of the highly ammoniated compounds evolve ammonia, with formation of less ammoniated products. In this way, the triammoniated chloride of copper becomes monammoniated, and the monammoniated chloride of zinc, $\frac{1}{2}$-ammoniated. The effects of a stronger heat upon the different compounds are very variable. Some, those of silver and calcium, for instance, give up all their ammonia, and leave metallic chloride; others undergo a reduction. Ammoniated chloride of cupricum, for instance, becomes chloride of cuprosum, whilst the ammoniated chlorides of nickel and platinosum leave metallic nickel and platinum respectively. The ammoniated chlorides of zinc $NH_3.2ZnCl$, and of mercury $NH_3.2HgCl$, however, are fusible and volatile without decomposition. The ammoniated nitrates, sulphates, and other salts, correspond generally to the chlorides. The compound metallicised ammoniums, which constitute the pseudo-metals of this class of salts, are for the most part transferable, by double decomposition, to a more complete extent than is generally supposed. Lea has recently obtained, for instance, several picrates of metallicised ammoniums, by double decomposition of their respective chlorides with picrate of ammonium. The individual salts of metallicised ammoniums will be described with their respective metals. The ammoniated compounds of bi-, ter-, and

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sesqui-equivalent metals are necessarily more complex in character than the compounds of protequivalent metals above referred to.

Oxidised Compounds of Nitrogen.

(265) The acids of nitrogen are in some respects anomalous. We have seen that the hydrides of chlorine and sulphur yield respectively a series of oxidised compounds, having well marked acid properties. In the same manner, the terhydride of phosphorus, a body corresponding in its formula and in many of its properties to ammonia, also yields a series of oxidised acid compounds, as shown in the third column of the table. Hence we should expect that ammonia would also yield oxacids, having the formulæ shown in the fourth column: —

HCl	H_2S	H_3P	H_3N.
$HClO$	——	——	——
$HClO_2$	——	H_3PO_2	——
$HClO_3$	H_2SO_3	H_3PO_3	H_3NO_3.
$HClO_4$	H_2SO_4	H_3PO_4	H_3NO_4.

But the oxidised compounds there indicated are not known to have any real existence. We are, however, acquainted with a few salts which may be regarded as derivatives from them, by the replacement of metal for hydrogen, thus: —

Pb_2HNO_3 Basic nitrite of lead.
Pb_2HNO_4, Pb_3NO_4 } Basic nitrates of lead.
$Bi'''NO_4$ Basic nitrate of bismuth.
Hg_3NO_4 Basic nitrate of mercuricum.
$_{,,}Hg_4HNO_4$ Basic nitrate of mercurosum.

These compounds, which are all crystalline, and with one exception all soluble in water, may be considered as normal nitrites and nitrates, or salts of orthonitrous and orthonitric acids respectively; and the oxacids of nitrogen, with which we are actually acquainted, may be conceived to result from these ortho-acids by the abstraction of an atom of water from each, thus: —

$H_3NO_3 - H_2O = HNO_2$ Nitrous acid. MNO_2 Nitrite.
$H_3NO_4 - H_2O = HNO_3$ Nitric acid. MNO_3 Nitrate.

We find, indeed, that the oxacids and oxisalts of phosphorus, which are normally tribasic, yield well-defined monobasic acids and salts, by the abstraction of an atom of water or an atom of base, as instanced particularly by phosphoric acid and the phosphates: —

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$H_3PO_4 - H_2O = HPO_3$ Metaphosphoric acid. MPO_3 Metaphosphate.

The difference between the phosphates and nitrates, quoad their modifications, seems to be that, as regards the former class, the orthophosphates are the ordinary salts, and the metaphosphates the exceptional; while, as regards the latter class, the orthonitrates are the exceptional, and what we may term the metanitrates the ordinary salts. It is observable, moreover, that nitric acid and the nitrates, in their comparative permanency, and in the completeness of their oxidation, do not correspond with normal teroxy-compounds, such as the chloric, sulphurous, and phosphorous acids and their salts, which are all easily oxidisable and easily reducible.

(266) Nitrites and nitrates are readily convertible into one another. Thus nitrites become nitrates by the action of oxidising agents, or by simply boiling their solutions in vessels allowing a free access of air. On the other hand, the nitrates of the alkali-metals are resolved by gentle ignition into nitrites and oxygen. Nitrites are also produced by the reducing action of certain metals upon the nitrates.

Nitrites and nitrates are procurable by the oxidation of ammonia; and, conversely, ammonia results from the hydrogenation of the nitrites and nitrates or their acids. Thus metallic zinc, when boiled in a strong solution of caustic potash to which a nitrite or nitrate has been added, evolves ammonia; while ammonia, passed over a heated mixture of lime and peroxide of iron, yields nitrate of calcium, &c.

Nitrous acid HNO_2, constitutes the aldehyd of nitric acid HNO_3, but we are unacquainted with the normal aldehyd of nitrous acid itself. Both chloraldehyds, however, ClNO and $ClNO_2$, are well known. By the action of water they are converted respectively into nitrous and nitric acids, by the usual exchange of peroxide of hydrogen for chlorine, thus: —

$$ClNO + H_2O = HCl + HNO_2$$
$$ClNO_2 + H_2O = HCl + HNO_3.$$

The radicle NO, or azotyl, unites with chlorine in two proportions to form the protochloride of azotyl ClNO, or nitrous chloraldehyd, and the bichloride of azotyl Cl_2NO, or chloronitric gas, as it has been termed. This compound exists largely in nitro-muriatic acid. It reacts with water to form both nitrous and nitric acids, thus: —

$$2Cl_2NO + 3H_2O = 4HCl + HNO_2 + HNO_3.$$

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Nitrogen forms a very complete series of oxides, as represented below: —

N_2O Nitrous oxide, or protoxide of nitrogen.
N_2O_2 Nitric oxide, or deutoxide of nitrogen.
N_2O_3 Nitrous anhydride.
N_2O_4 Pernitric oxide, or nitroso-nitric anhydride.
N_2O_5 Nitric anhydride.

All these compounds are directly or indirectly procurable from nitric acid, and reconvertible thereinto. The three higher oxides or anhydrides are decomposed by water, to form their corresponding acids, thus: —

$$N_2O_3 + H_2O = 2HNO_2 \text{ nitrous acid.}$$
$$N_2O_4 + H_2O = HNO_2 + HNO_3 \text{ nitrous and nitric acids.}$$
$$N_2O_5 + H_2O = 2HNO_3 \text{ nitric acid.}$$

But the nitrous acid resulting from the first and second reactions is itself a very unstable substance, and, by excess of water, is decomposed into nitric acid, nitric oxide, and water, thus: —

$$3HNO_2 = HNO_3 + N_2O_2 + H_2O.$$

Nitrous Oxide.

Symbol, N_2O; *Proportional number,* 44; *Density,* 22; *Atomic volume,* □□.

(267) This gas, also known as protoxide of nitrogen, cannot be formed by the direct combination of its constituent elements. It results, not only from the processes usually employed for its preparation, but also from many reactions, in which the higher oxides of nitrogen undergo reduction. It was discovered by Priestley in 1776, and minutely examined by Davy in 1809, who first noticed the lively stimulant effects produced by its inhalation, whence its popular name of laughing gas.

a. Nitrate of ammonium is gently heated in a flask or retort, to a temperature not exceeding 250°, when it puts on the appearance of ebullition, and is entirely decomposed into water and nitrous oxide: —

$$NH_4NO_3 - 2H_2O = N_2O.$$

The gas may be collected over brine, warm water, or mercury. When the temperature of the fused salt is allowed to get too high, a much more complex decomposition ensues, attended with the

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evolution of white fumes of nitrate and nitrite of ammonium, and of nitrogen, nitric oxide, and ammoniacal gases. Moreover, this decomposition is sometimes attended with explosion. The nitrate of ammonium employed to yield laughing gas should be free from any trace of chloride of ammonium, otherwise the product will be contaminated with chlorine.

β. When granulated zinc is acted upon by nitric acid diluted with eight or ten times its volume of water, very pure nitrous oxide gas is slowly evolved: —

$$10HNO_3 + Zn_8 = 8ZnNO_3 + 5H_2O + N_2O.$$

γ. Nitrous oxide may also be prepared by decomposing nitric acid, or a nitrate, with a chlorhydric acid solution of stannous chloride; by acting upon sal-ammoniac with nitric acid of sp. gr. 1·2; by slowly passing nitric oxide gas through a solution of sulphurous acid or an acid sulphite; by decomposing nitrosulphate of ammonium with water; and by many other reactions.

(268) Nitrous oxide has been obtained in the liquid state by direct mechanical compression of the gas, and by decomposing nitrate of ammonium in one limb of a bent sealed tube; but this last method is dangerous and otherwise unsatisfactory, owing to the difficulty with which the salt decomposes when subjected to considerable pressure. Solid nitrous oxide results from the spontaneous evaporation of the liquid, and also from exposing it to the action of a freezing mixture of solid carbonic anhydride and ether. Solid nitrous oxide occurs as a white snow-like mass, which melts at about $-100°$. When placed on the hand, it quickly liquefies and evaporates, leaving a blister resembling that caused by a burn. Mixed with bisulphide of carbon, and evaporated in vacuo, it effects a depression of the thermometer to $-140°$, the lowest point of temperature which has been hitherto attained. Liquid nitrous oxide is a colourless, very mobile fluid, of extremely low refractive power. When dropped on the hand, it instantly evaporates, leaving a blister. Under a pressure of 50 atmospheres, and at the temperature of 7°, its sp. gr. was found to be 0·908. It boiled at about $-88°$. The low temperature produced by the evaporation in vacuo of bisulphide of carbon and liquid nitrous oxide is very little above that obtained by means of the solid oxide. Nitrous oxide gas is colourless and feebly refrangible. It has a slight agreeable odour, and pleasant, sweetish taste. When respired for a period of four or five minutes, it produces a lively intoxication, often attended with a disposition to muscular exertion and violent laughter. Animals

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immersed in the gas become restless, and die after some time. Nitrous oxide is somewhat soluble in water, 100 measures of which absorb 130 volumes of the gas at 0°, 78 volumes at 15°, and 61 volumes at 24°. It is still more soluble in alcohol, 100 measures of which absorb 418 volumes of the gas at 0°, 327 volumes at 15°, and 285 volumes at 24°. It also dissolves in ether, and in the fixed and volatile oils. Neither the gas nor any of its solutions has any action upon vegetable colours. Nitrous oxide is decomposed by a series of electric sparks, or by transmission through a red-hot tube, into one volume of oxygen and two of nitrogen. It forms explosive mixtures with many inflammable gases. When exploded with its own volume of hydrogen, it is decomposed into water and a quantity of nitrogen equal in bulk to the original gas. Nitrous oxide acts like oxygen as a supporter of combustion, but, unlike oxygen, is not affected by admixture with nitric oxide. A glowing match introduced into the gas bursts into flame, and burns with a brilliancy almost equal to that which it manifests in oxygen. Ignited carbon and its compounds inflame very readily in nitrous gas; but other combustibles, phosphorus and sulphur, for instance, require to be strongly heated in order to burn. Their combustion, when once established, however, takes place with great brilliancy. Sodium, heated in nitrous oxide, takes fire and leaves a volume of nitrogen equal to that of the original gas. Iron, zinc, and other metals, when in a state of ignition, also continue to burn in nitrous oxide.

Nitric Oxide.

Symbol, N_2O_2, or $(NO)_2$; *Proportional number*, 60; *Density*, 15; *Atomic volume*, ⊞.

(269) This gas, also known by the names azotyl, nitrosyl, and deutoxide or binoxide of nitrogen, was first investigated, if not discovered, by Priestley. It may be prepared thus: — *a*. By acting upon copper clippings or borings with nitric acid of sp. gr. 1·2, made by diluting the strong acid with about twice its bulk of water: —

$$Cu_3 + 4HNO_3 = 3CuNO_3 + 2H_2O + NO.$$

Should the reaction not take place at once, it may be set up by the application of a gentle heat, but the lower the temperature the purer the resulting gas. When strong nitric acid is used, or when a high temperature is permitted, the nitric oxide is contaminated

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to a considerable extent with nitrogen. Other metals—lead, mercury, silver, and bismuth, for instance—may be substituted for copper in the above reaction, but with them a stronger acid or a higher temperature is required. *β.* Nitric oxide may also be obtained abundantly, and in a pure state, by decomposing nitre with a solution of ferrous chloride in chlorhydric acid, or of ferrous sulphate in dilute sulphuric acid: —

$$6Fe_2SO_4+5H_2SO_4+2KNO_3=3\{Fe_4(SO_4)_3\}+2HKSO_4+4H_2O+N_2O_2.$$

γ. Nitric oxide, more or less pure, results from many other reductions of nitrous or nitric acid; and also from the oxidation of ammonia, as when that gas is passed over heated oxide of manganese, for instance.

(270) Nitric oxide is a colourless gas, very sparingly soluble in water, so that it may be collected over the hydro-pneumatic trough. According to Henry, one volume of water at mean temperature absorbs $\frac{1}{20}$ of its volume of the gas. According to Bunsen, 100 volumes of alcohol at 15° absorb 27·4 volumes of the gas. Nitric oxide has not been liquefied. It is a very stable compound, and, if perfectly dry, is not decomposed by a red heat, or by the action of electric sparks. It combines directly with free oxygen to produce deep orange-brown fumes, of variable composition, which dissolve in water to form an acid solution, the gas itself, however, being perfectly neutral to vegetable colours. From the characteristic nature of this reaction, nitric oxide may be advantageously employed to detect the presence of free oxygen in any gaseous mixture. It was formerly used, especially by Priestley and Cavendish, to estimate the proportion present, but for this purpose it has been superseded by more trustworthy reagents. Owing to its rapid union with oxygen and formation of acid products, its actual taste, smell, and respirability have not been ascertained. Nitric oxide gas is absorbed freely by nitric acid, with probable conversion into pernitric oxide, and formation of a deep-brown, green, or blue liquid, according to the concentration of the acid. Solutions of protosalts of iron absorb nitric oxide, with production of a deep brownish-green, almost black colour. This brown liquid contains eight atoms of iron to each molecule of nitric oxide, thus: — $4Fe_2SO_4 . N_2O_2$. When heated, it gives up nearly the whole of the absorbed gas; but, by exposure to air, it becomes rapidly oxidated. Precisely similar compounds are formed with solutions of chromous salts and nitric oxide. Stannous and mercurous salts also absorb

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nitric oxide, but with mutual decomposition. Nitric oxide forms crystalline compounds with stannic chloride, and with sulphuric acid or anhydride.

Moist nitric oxide gas is decomposed by a succession of electric sparks into nitrogen and nitric acid. It is slowly converted by moist iron filings, zinc filings, soluble sulphides, acid sulphites, stannous chloride, and other reducing agents, into nitrous oxide, which is frequently accompanied with ammonia. Nitric oxide is completely converted into ammonia when mixed with excess of sulphydric acid and transmitted over heated quicklime. A mixture of moist iron filings and sulphur also reduces nitric oxide very completely, but chiefly to the state of free nitrogen. On the other hand, nitric oxide is, as it were, oxidated by the peroxides of lead and manganese, and the protoxide of silver, so as to form nitrites of the respective metals, accompanied in the last case with a liberation of silver. Ordinary combustibles do not burn in nitric oxide, but phosphorus and carbon, when introduced in full combustion, burn in the gas with very great brilliancy. Four volumes of nitric oxide, passed over red hot charcoal, are converted into two volumes of nitrogen and two of carbonic anhydride. Sulphur does not burn in nitric oxide, but a mixture of bisulphide of carbon vapour and nitric oxide gas inflames readily, producing a bright greenish flash of light. Red-hot iron decomposes nitric oxide, with liberation of half its volume of nitrogen. Potassium and sodium effect similar decompositions when heated sufficiently to burn in the gas.

The molecule of nitric oxide $(NO)_2$, like that of sodium, Na_2, is binary or dyadic. Like sodium also, nitric oxide has been introduced into several compounds as a substitute for hydrogen, to which it is equivalent atom to atom. Thus we have alcohol C_2H_6O, ethylate of sodium C_2H_5NaO, and nitroso-alcohol or nitrous ether $C_2H_5(NO)O$. Again, we have sulphuric acid H_2SO_4, acid sulphate of sodium $HNaSO_4$, and acid sulphate of azotyl $H(NO)SO_4$. The atom of nitric oxide has for the most part a chlorous rather than a basylous function, but it is, nevertheless, capable of displacing basylous hydrogen, as shown in the above examples. The correlations of nitric oxide, chloride of azotyl, nitrous acid, and nitrous anhydride, correspond to those of sodium, chloride of sodium, hydrate of sodium, and oxide of sodium, thus:

Na_2	NaCl	NaHO	Na_2O.
$(NO)_2$	(NO)Cl	(NO)HO	$(NO)_2O$.

According to Weltzien, the atom of nitric oxide NO, is sometimes

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diequivalent, or capable of displacing two atoms of hydrogen, a view which the circumstance of its uniting with chlorine in two proportions, to form a protochloride and a bichloride respectively, renders extremely probable.

(271) CHLORIDE OF AZOTYL. *Sym.* NOCl.; *p.n.* 65·5; *v. d.* 32·75; □□.—This compound, also called chloro-nitrous gas, constitutes the chloraldehyd of nitrous acid HNO_2. *a.* It results from the direct combination of chlorine and nitric oxide gases. One volume of the former and two of the latter unite to form two volumes of chloride of azotyl. *β.* It also constitutes the principal product of the latter stage of the decomposition of nitro-muriatic acid.

Chloride of azotyl is a deep orange-coloured gas. It is condensed by a freezing mixture of salt and ice, into a red fuming liquid, possessing the peculiar smell of aqua regia. Like chloraldehyds in general, it is decomposed by water into chlorhydric acid, and the special acid to which it appertains, in this case, the nitrous. It reacts in a similar manner with an alkaline hydrate, forming a chloride and nitrite of alkali-metal:—

$$NOCl + 2KHO = KCl + K(NO)O + H_2O.$$

It is decomposed by mercury, with formation of calomel and liberation of nitric oxide:—

$$NOCl + Hg_2 = Hg_2Cl + NO.$$

It is without action upon gold or platinum.

(272) BICHLORIDE OF AZOTYL. *Sym.* $NOCl_2$; *p.n.* 101.—This compound, called by its discoverer, Gay Lussac, chloro-nitric gas, is made by distilling at a gentle heat, in a water bath, a mixture of one part of strong nitric with about three parts of chlorhydric acid. The products should first be passed through a vessel surrounded by ice, in order to deposit any volatilized acids, and then through a U-tube immersed in a freezing mixture of salt and ice. In this tube, the compound condenses, while free chlorine passes off in the gaseous state:—

$$HNO_3 + 3HCl = NOCl_2 + 2H_2O + Cl.$$

Bichloride of azotyl is obtained as a transparent, red, fuming liquid, which may be dried over chloride of calcium. It boils at − 7°, being converted into a deep lemon-yellow gas or vapour, smelling strongly of aqua regia. When decomposed by alkaline hydrates, it forms a nitrate as well as a nitrite and chloride of alkali-metal, thus:—

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$$2NOCl_2 + 6KHO = 4KCl + KNO_2 + KNO_3 + 3H_2O.$$

It reacts in a similar manner with water, producing nitrous, nitric, and chlorhydric acids. With excess of mercury it produces calomel and nitric oxide. It is without action on gold or platinum.

(273) AQUA REGIA, or nitro-muriatic acid, is a yellow fuming corrosive liquid, made by mixing strong nitric and chlorhydric acids. The mixture is at first colourless, but after a short time, or quickly if heated, assumes a deep orange-yellow colour, and breaks up into water, chlorine, and the chlorides of azotyl, principally the bichloride. The dilute acids may remain in admixture for a long time without decomposing each other, unless heat be applied. The solvent action of nitro-muriatic acid upon gold and platinum, for which it is principally employed, seems to depend entirely upon the presence of the chlorine liberated by the mutual reaction of the two original acids. An impure aqua-regia is made by dissolving nitrate of sodium in chlorhydric acid, or even chloride of sodium in nitric acid. Nitrates, when acted upon by an excess of chlorhydric acid, are completely converted into chlorides; and most chlorides, when acted upon by an excess of nitric acid, are completely converted into nitrates, with formation, in each case, of chlorine and the chlorides of azotyl.

NITROUS ANHYDRIDE, ACID, AND SALTS.

(274) The mutual relations of this acid and anhydride correspond to those of sulphurous acid and anhydride; that is to say, the acid may be converted into the anhydride by the simple abstraction of water, effected by ordinary desiccating agents: —

$$2HNO_2 - H_2O = N_2O_3.$$

Moreover, the acid itself is a very unstable compound at ordinary temperatures, and, on dilution with much water, is decomposed into nitric acid, water, and nitric oxide: —

$$3HNO_2 = HNO_3 + H_2O + N_2O_2.$$

Hence, when an excess of water reacts upon nitrous anhydride, we obtain, not nitrous acid, but nitric acid, together with nitric oxide gas. Nitrous acid, however, is soluble in ice-cold water, and in aqueous nitric acid, apparently without change. The nitrites MNO_2, are well defined and moderately stable salts. When nitrous acid or anhydride reacts upon an acidulous, neutral, or basylous hydrate,

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nitroso-compounds, in which an atom of hydrogen is displaced by one of nitrosyl, are usually produced. But the most interesting reactions of nitrous acid or anhydride are those which it effects upon amine- or amide-compounds. According to Piria's reaction, an aqueous solution of an amine or amide, when treated with nitrous acid or anhydride, yields the acidulous constituent of the ammoniacal salt, from which it might have been formed by an elimination of water. Thus phenylamine is produced by very many processes, among others by abstracting water from phenylate of ammonia, thus: —

$$C_6H_6O + NH_3 - H_2O = C_6H_5(H_2N).$$

Now when this compound, or a salt thereof, is acted upon by nitrous acid or anhydride, we have the following reaction, which is one of very considerable generality: —

$$C_6H_5(H_2N) + HNO_2 = C_6H_6O + H_2O + N_2.$$

But Griess has found that when nitrous acid or anhydride is passed into alcoholic solutions of amines or amides, a different or intermediate reaction takes place, attended with the formation of compounds, in which one atom of nitrogen displaces three of hydrogen. Thus the double molecule of phenylamine reacts with nitrous acid or anhydride, according to the following equation, and similarly in many other instances: —

$$C_{12}H_{10}(H_4N_2) + HNO_2 = C_{12}H_{10}(HN_3) + 2H_2O.$$

(275) NITROUS ANHYDRIDE. *Sym.* N_2O_3; *p.n.* 76.—*a.* When dry oxygen gas is added to a large excess of dry nitric oxide, four volumes of the latter combine with one volume of the former to produce brownish red vapours, which may be condensed by a freezing mixture of salt and ice. *β.* Nitrous anhydride (or acid) may also be made by adding a small quantity of ice-cold water to liquid peroxide of nitrogen, surrounded by a freezing mixture. After the reaction of the two has taken place, distillation may be effected at a low temperature, and the product condensed in a U-tube immersed in salt and ice. *γ.* Or the vapours produced by deoxidating nitric acid with arsenious anhydride or starch, may be dehydrated by transmission over chloride of calcium, and condensed in a U-tube immersed in the same freezing mixture. Nitrous anhydride occurs as a very volatile blue liquid, which reacts with a small quantity of water to form nitrous acid, but with a larger quantity is rapidly decomposed into nitric acid and nitric oxide; unless,

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indeed, the temperature of the mixture be kept at or below zero, when the pale blue-coloured solution of nitrous acid is tolerably permanent.

(276) NITROUS ACID. *Sym.* HNO_2; *p.n.* 47.—*a.* This is an ill-defined compound, which most probably constitutes the bluish liquid resulting from the action of a small quantity of ice-cold water upon nitrous anhydride. *β.* When nitric acid reacts at a gentle heat upon arsenious anhydride, we have the following reaction: —

$$As_2O_3 + 3H_2O + 2HNO_3 = 2H_3AsO_4 + 2HNO_2, \text{ or } H_2O.N_2O_3.$$

Deep brown vapours are given off, which are supposed to be the acid, but which may possibly, at the temperature employed, be only the moist anhydride; at any rate, by transmission over chloride of calcium, the water is abstracted, and the anhydride left. Similar vapours are given off by acting upon starch with a large excess of nitric acid, sp. gr. 1·25; but the process is attended with considerable frothing, and occasionally, when a stronger acid is employed, with explosion. *γ.* Nitrous acid is liberated from its salts by the action of nearly any other acid; but most frequently it is no sooner liberated than decomposed into nitric acid, water, and nitric oxide. Ice-cold acidified solutions of nitrites, however, that of nitrite of potassium with sulphuric acid for instance, seem to contain undecomposed nitrous acid.

Nitrous acid, or rather the acidulated solution of a nitrite, acts very readily both as a reducing and an oxidising agent. Thus it reduces permanganic and chromic acids to the state of manganous and chromic salts, and mercurous and auric salts, even to the metallic state. On the other hand, it bleaches indigo by oxidation, liberates iodine from iodide of potassium, and converts ferrous into ferric salts, with production of nitric oxide. The facility with which these reactions are effected enables us easily to ascertain the presence of nitrous acid or a nitrite. Thus the solution of a nitrate may be added, without any visible effect, to a weak solution of iodide of potassium, slightly acidulated with chlorhydric acid and mixed with starch; but should it contain any nitrite, a deep blue colour is at once produced. Again, the solution of a nitrate may be added, without any visible effect, to sulphate of iron dissolved in cold dilute sulphuric acid; but should it contain any nitrite, a brownish green discolouration is at once produced.

(277) NITRITES. *Sym.* MNO_2. — *a.* When oxygen gas is added little by little to nitric oxide standing over a solution of potash, the

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nitric oxide is gradually and completely absorbed, with formation of nitrite of potassium KNO_2. Nitrites also result from passing nitric oxide over metallic peroxides, as before referred to. β. Nitrites are usually made by reducing nitrates, by fusing metallic lead with soda- or potash-nitre, for instance. The nitrates of potassium and sodium, also, when merely heated to redness for a short time, give off oxygen, and leave residues consisting principally of nitrite. Again, when metallic lead is boiled in solution of nitrate of lead, we obtain the basic or orthonitrite, thus: —

$$2PbNO_3 + Pb_2 + H_2O = 2Pb_2HNO_3, \text{ or } 2(PbNO_2 . PbHO).$$

γ. The sparingly soluble nitrites of silver and lead may be precipitated from the nitrites of sodium and potassium by double decomposition. δ. Nitrites are frequently found in the well-waters of towns, and are then probably formed by an oxidation of ammonia. Platinum-black speedily converts a mixture of ammonia and atmospheric air into nitrite of ammonium. A coil of heated platinum wire, introduced into a flask of air to which a few drops of strong ammonia have been added, also produces an instantaneous cloud of nitrite of ammonium. Again, when finely divided metallic copper is shaken with moist ammoniacal air, a rapid oxidation of the metal into oxide of copper, and of the ammonia into nitrite of copper takes place.

The nitrites are colourless, or slightly yellow, crystallisable salts, which are generally anhydrous. When heated they fuse, but on cooling solidify unchanged. When strongly heated, however, they undergo decomposition, evolving a mixture of oxygen and nitrogen gases. They detonate sharply when heated with combustible bodies. Normal nitrites are all soluble in water, those of lead and silver, however, being but sparingly soluble. These last two salts may be readily purified by dissolving them in hot water, from which they crystallise out on cooling. The nitrites of potassium, calcium, magnesium, and manganese are deliquescent. The sodium and potassium-salts have an alkaline reaction to test paper (Rose). Dissolved nitrites react with aqueous sulphate of copper to produce nitrite of copper, which forms a peculiar and very characteristic apple-green solution. Heated solutions of nitrites, exposed to the air, absorb oxygen to become converted into nitrates. When boiled for a long time in a flask or retort, they are decomposed, yielding nitrate, nitric oxide, and free alkali: —

$$3KNO_2 + H_2O \doteq KNO_3 + 2KHO + N_2O_2.$$

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The nitrites, like nitrous acid, act readily both as oxidising and reducing agents.

Pernitric Oxide.

Symbol, N_2O_4, *or* $(NO_2)_2$; *Proportional number*, 92; *Vapour density*, 23; *Atomic volume*, ⊞.

(278) *α.* This is the principal constituent of the orange fumes produced by mixing nitric oxide with oxygen or air. When nitric oxide is mixed with an excess of oxygen, four volumes of the former combine with two of the latter gas to become condensed into four volumes of pernitric oxide. When a mixture of four volumes of nitric oxide, and two volumes of oxygen, incorporated by passing through a tube filled with broken porcelain, and thoroughly dried by transmission over pumice soaked in oil of vitriol, and then over recently fused stick potash, is submitted to the action of a freezing mixture of salt and ice, pernitric oxide condenses into transparent crystals; or, if the slightest trace of moisture be present, into an almost colourless liquid. *β.* When thoroughly dried nitrate of lead is heated in a glass retort, it evolves a mixture of pernitric oxide and oxygen gases, the former of which may be condensed by a freezing mixture of salt and ice, while the latter passes on:—

$$2PbNO_3 = Pb_2O + O + N_2O_4.$$

The first portions of pernitric oxide thus obtained do not solidify, doubtless owing to the presence of a trace of moisture; but if the receiver be changed in the midst of the operation, and if every care has been taken to avoid moisture, the later portions may be obtained in the crystalline form.

(279) Pernitric oxide occurs in transparent colourless prismatic crystals, which melt at −9°, but which, when once melted, do not resolidify until cooled down to −30°. Above −9°, pernitric oxide forms a mobile liquid, of sp. gr. 1·451, the appearance of which varies greatly according to the temperature. When still liquid below −9°, it is almost colourless; at −9°, it has a perceptible greenish-yellow tint; at 0°, the colour is somewhat more marked; at 10°, it is decidedly yellow; and at 15°, and upwards, orange-yellow; the depth of colour increasing progressively with the temperature up to 22°, the boiling point of the liquid. Pernitric oxide vapour has a brown red colour, the depth of which also increases with the temperature, until at 40°, it is so dark as to be almost opaque. Liquid pernitric oxide gives off at ordinary tem-

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peratures an abundance of reddish vapours, which, when mixed with air, are extremely difficult to condense. These vapours, which have a pungent suffocating odour and acid taste, are quite irrespirable. They stain the skin of a bright yellow.

Pernitric oxide is decomposed by water, with production of nitrous and nitric acids, whence it may be looked upon as nitroso-nitric anhydride:—

$$N_2O_4 + H_2O = HNO_2 + HNO_3.$$

To secure this simple decomposition, the reaction must be effected at a very low temperature. If to pernitric oxide, cooled by ice and salt, a small quantity of ice-cold water be added, two layers of liquid are formed, the upper and least coloured of which consists principally of aqueous nitric acid, the lower and darker coloured one of nitrous acid and anhydride, which may be distilled off at a low temperature, as before referred to. In a similar manner, pernitric oxide reacts upon caustic alkalies, when not too dilute, with formation of a nitrate and nitrite of alkali-metal.

But when pernitric oxide is added to an excess of water, at ordinary temperatures, it is decomposed into nitric acid, and the products of the decomposition of nitrous acid, namely, nitric acid, water, and nitric oxide gas. As the quantity of pernitric oxide added to the water increases, the evolution of nitric oxide gas becomes less and less obvious, until, when a considerable quantity of nitric acid has been formed, it disappears altogether. During this saturation of the water with nitric acid, it becomes successively blue, green, and orange-coloured. These colours depend upon the solution of unaltered pernitric oxide in the aqueous nitric acid, which, according to its concentration, is capable of dissolving an increasing quantity, and of decomposing a decreasing quantity of the compound. The similarly coloured liquids produced by treating aqueous nitric acid with nitric oxide gas, are also thought to owe their colour to the presence of pernitric oxide, formed by deoxidating a portion of the nitric acid:—

$$N_2O_2 + 4HNO_3 = 2H_2O + 3N_2O_4.$$

Pernitric oxide is not decomposed at a dull red heat. Mixed pernitric oxide and hydrogen gases, passed over spongy platinum, react upon one another with production of water and ammonia, the platinum at the same time becoming red-hot. Pernitric oxide is also absorbed by aqueous sulphydric acid, with formation of ammonia and deposition of sulphur. Ordinary combustibles

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are extinguished by pernitric oxide vapour; but charcoal and phosphorus, when strongly ignited, burn in it with considerable brilliancy, and liberate its nitrogen. It is also decomposed by iron and other metals, at a red heat, with liberation of nitrogen. Potassium, introduced into the vapour at ordinary temperatures, inflames spontaneously, and burns with a red flame. Pernitric oxide usually reacts with basylous metallic oxides, as before observed, to form mixtures of nitrite and nitrate; but it seems also to unite directly with some double oxides to form definite double salts, such as cobalt yellow $CoKO.N_2O_4$, the intimate constitution of which is not well understood. The molecule of pernitric oxide, $(NO_2)_2$, like that of a halogen, bromine, for instance, Br_2, is binary or dyadic. Guthrie, moreover, has shown that its molecule, like that of bromine, can combine directly with hydrocarbons, while its atom can displace directly an atom of hydrogen. Thus amylene C_5H_{10}, combines directly with bromine and pernitric oxide respectively, to form the compounds $C_5H_{10}Br_2$, and $C_5H_{10}(NO_2)_2$. Again, naphthalene $C_{10}H_8$, reacts with bromine and pernitric oxide respectively to form the compounds $C_{10}H_7Br$, and $C_{10}H_7(NO_2)$. The correlations of pernitric oxide, chloride of nitryl, nitric acid, and nitric anhydride, correspond to those of nitric oxide, chloride of azotyl, nitrous acid, and nitrous anhydride, thus:—

$(NO)_2$	$(NO)\,Cl$	$(NO)\,HO$	$(NO)_2\,O$
$(NO_2)_2$	$(NO_2)Cl$	$(NO_2)HO$	$(NO_2)_2O$.

Nitro-derivatives, such as nitro-naphthalene, for instance, $C_{10}H_7(NO_2)$, are made most readily, not from pernitric oxide, but from nitric acid, precisely as azotyl derivatives are made most readily, not from nitric oxide, but from nitrous acid or anhydride:—

$$C_{10}H_8 + HNO_3 = C_{10}H_7(NO_2) + H_2O.$$

Nitro-derivatives are known, in which two, three, four, and even more atoms of hydrogen are displaced by peroxide of nitrogen. Pernitric oxide is more decidedly chlorous in its habitudes than is nitric oxide.

(280) Chloride of Nitryl. — *Sym.* $ClNO_2$; *p. n.* 81·5. — This compound is produced by the action of phosphoric chloraldehyd upon nitrate of lead, according to the equation:—

$$3PbNO_3 + PCl_3O = Pb_3PO_4 + 3NO_2Cl.$$

It is also formed by the action of Williamson's chlorhydrosulphurous acid upon nitre, thus:—

$$KNO_3 + HClSO_3 = KHSO_4 + NO_2Cl.$$

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It occurs as a thin pale oil, smelling somewhat of aqua regia. It is decomposed by water, after the manner of chloraldehyds, into chlorhydric and nitric acids:—

$$NO_2Cl + H_2O = HCl + HNO_3.$$

It has not been minutely examined.

Nitric Anhydride, Acid, and Salts.

(281) Nitric Anhydride. *Sym.* N_2O_5; *p.n.* 108.—This compound, first obtained by Deville, in 1848, was prepared by acting upon nitrate of silver with dry chlorine gas, the final result of the reaction being as follows:—

$$2AgNO_3 + Cl_2 = 2AgCl + N_2O_5 + O.$$

Chlorine gas is first collected in a large glass gas-holder, charged with sulphuric acid instead of water. Then, by allowing sulphuric acid to flow slowly into the holder, a gradual current of chlorine is obtained, which is passed successively over chloride of calcium, over pumice soaked in oil of vitriol, and over nitrate of silver contained in a U-tube immersed in a water-bath. The nitrate of silver is first heated to a temperature of 95°, but after the action has once commenced, is kept steadily at 60°. The products of the reaction pass into a second U-tube, connected by fusion with the one containing the nitrate of silver, and having a narrow necked bulb attached to its lowest portion. In this tube, surrounded by a freezing mixture of salt and ice, two substances are collected, the one, liquid, which flows into the bulb, the other solid, which condenses in the limbs of the tube. The liquid product, probably some lower oxide of nitrogen, may be driven off in a current of carbonic anhydride. The solid product constitutes nitric anhydride. Its composition may be determined by estimating the quantity of nitrogen produced by volatilising it over red-hot metallic copper, whereby its oxygen is abstracted. Nitric anhydride occurs in colourless rhombic prisms, with angles of about 60 and 120°, and in hexagonal prisms derived therefrom. It melts at 19°—20°, and boils at 45°—50°, near to which temperature, however, it undergoes decomposition. Hence its vapour-density has not been ascertained. Its reaction upon water takes place with a considerable evolution of heat, and formation of nitric acid, unaccompanied by any other nitrogen compound:—

$$N_2O_5 + H_2O = 2HNO_3.$$

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The crystals may be preserved for any length of time in the cold, but in warm weather they liquefy and undergo decomposition.

(282) NITRIC ACID. *Sym.* HNO_3; *p.n.* 63; *v. d.* 31·5; □□.—*a.* When nitrogen gas, mixed with ten or twelve times its bulk of hydrogen, is burnt in air or oxygen, the resulting water is found to contain, in addition to nitrate of ammonium, a small quantity of free nitric acid. Again, when a succession of electric sparks is passed through a moist mixture of two volumes of nitrogen and five of oxygen, traces of nitric acid are slowly formed. Cavendish first ascertained the composition of nitric acid by a modification of this experiment. Davy noticed that traces of nitric acid were produced at the positive pole, when water containing atmospheric air was submitted to electrolysis.

β. Nitric acid results from the decomposition of nitrous acid, and of all the oxides of nitrogen. Thus traces of nitric acid are formed from moist nitrous and nitric oxide gases, by transmission through red-hot tubes, or by electrisation; while quantities of it are produced by the action of water upon the nitrous, nitroso-nitric, and nitric anhydrides. Nitric acid also occurs among the products resulting from the transmission, through red-hot tubes, of an excess of oxygen mixed with ammoniacal or moist cyanogen gas.

γ. Nitric acid is always prepared, both for manufacturing and laboratory purposes, by the action of sulphuric acid upon a nitrate, usually nitrate of sodium:—

$$H_2SO_4 + NaNO_3 = HNaSO_4 + HNO_3.$$

For laboratory purposes, the process may be performed in a large glass retort, into which nitrate of sodium, with rather less than an equal weight, or nitrate of potassium with about an equal weight, of sulphuric acid is introduced. The reaction takes place at a gentle heat, and the product may be easily condensed in a receiver kept cool by water. At the beginning of the operation, some red fumes are often evolved, owing to the large excess of sulphuric acid then existing, producing a decomposition of the liberated nitric acid into water, oxygen, and pernitric oxide. A similar appearance often takes place at the close of the operation, owing to a similar decomposition of the last portions of nitric acid by the increased heat required to drive them over.

Nitric acid is produced on a manufacturing scale by distilling nitrate of sodium and sulphuric acid in large horizontal iron cylinders, and collecting the distillate in a series of stoneware

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Woulfe's bottles, into the last of which a certain quantity of water is poured, to effect a complete condensation. The proportion of nitrate of sodium used is generally much greater than that above indicated, so that two successive reactions have to be effected, thus:—

1°. $H_2SO_4 + 2NaNO_3 = HNaSO_4 + HNO_3 + NaNO_3$.
2°. $HNaSO_4 + NaNO_3 = Na_2SO_4 + HNO_3$.

The first reaction, resulting in the formation of acid sulphate of sodium, and liberation of half the nitric acid, takes place readily, at a moderate temperature. The second reaction, consisting in the mutual decomposition of the acid sulphate of sodium and remaining nitrate of sodium, requires a much higher temperature, whereby the distillate is contaminated to a considerable extent with peroxide of nitrogen. The acid condensed in the first Woulfe's bottle usually contains chlorine, from the presence of chlorides in the nitre employed, and also traces of sulphuric acid carried over mechanically; but the contents of the intermediate bottles are usually very pure. The contaminated acid may be purified, if necessary, by distilling it off a little fresh nitre, to hold back the sulphuric acid. All the chlorine and peroxide of nitrogen pass over with the earlier portions, and by changing the receiver as soon as the distillate ceases to produce any turbidity with nitrate of silver solution, a pure acid may be collected. Nitric acid is ordinarily purified from peroxide of nitrogen by heating it for a short time to its boiling point. Millon prepared a very strong and pure acid by distilling off the first third of the ordinary acid, adding to the residue an equal weight of oil of vitriol, continuing the distillation, and collecting the product separately. After re-distilling the greater portion of the product, to free it from any sulphuric acid, he heated it to the boiling point, and passed a current of dry carbonic anhydride through it until it became cold. He thus obtained a strong colourless acid, free alike from water and peroxide of nitrogen.

(283) Nitric acid is a colourless, transparent, mobile liquid, of sp. gr. 1·52. It freezes at about −55° into a buttery mass. It boils at 86°, with partial decomposition, leaving a weaker acid behind. Transmission through a red-hot tube, or exposure to the light of the sun, produces a similar decomposition of the strong acid into water, peroxide of nitrogen, and oxygen. Nitric acid exerts a highly corrosive action on organic bodies, and, even when somewhat diluted, stains the nitrogenous tissues of a bright yellow colour.

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In the presence of moist air, nitric acid gives off opaque white vapours, having a characteristic odour and sour taste. It absorbs water from the atmosphere, but with less avidity than sulphuric acid. Its admixture with water is accompanied with a sensible development of heat, and formation of a definite sesquihydrate, represented by the formula $2NHO_3.3H_2O$. It is a colourless, strongly acid liquid, having a sp. gr. 1·42. It boils at 123°, without decomposition. Weaker and stronger acids are alike reduced to this state of hydration by boiling, the weaker acids losing water, and the stronger acids the elements of nitric anhydride. According to Bineau's determination, the vapour-density of this hydrate corresponds to that of four volumes of nitric acid and six volumes of steam united without condensation.

Nitric acid, especially when heated, is a most powerful oxygenant, and acts more or less violently upon all the solid non-metallic elements. It converts iodine, sulphur, selenium, tellurium, phosphorus, arsenic, boron, carbon, and silicon, into iodic, sulphuric, selenious, tellurous, phosphoric, arsenic, boric, carbonic, and silicic acids respectively. Finely powdered charcoal, if perfectly dry, manifests a species of deflagration when moistened with the strong acid, and ignited charcoal undergoes a brilliant combustion. All metals, with the exception of titanium, tantalum, gold, platinum, and some of its congeners, are attackable by nitric acid. Tin, antimony, and tungsten, when heated with the moderately strong acid, are oxidated into the insoluble stannic, antimonic, and tungstic anhydrides. The other metals, and tin also when a weak acid is used, are converted into nitrates. The action of nitric acid upon the metals varies with its temperature, concentration, and purity. The pure acid, whether strong or dilute, when surrounded by a mixture of salt and ice, acts readily upon metallic zinc, but is without action upon copper. Even at ordinary temperatures, pure nitric acid diluted to the sp. gr. 1·10, does not attack copper, but requires to be heated to 20° and upwards. The addition of a few drops of nitrite of sodium solution, however, establishes a rapid action at 15°, and even lower. Silver and mercury are not attacked by pure nitric acid of a sp. gr. inferior to 1·42, save at an increased temperature, or in the presence of nitrous acid. Bismuth and tin, on the contrary, preserve their brilliancy in strong nitric acid, but are attacked with violence on the addition of a little water. The behaviour of iron is still more curious. This metal is readily acted upon by the dilute, but preserves its metallic aspect unchanged when immersed in the concentrated acid; and even the subsequent addition of water is not

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productive of any effect. But if it be then touched with a more electro-negative metal, platinum, silver, or copper, for instance, it loses its passive state immediately, and is rapidly attacked by the diluted acid.

The degree of reducing action exerted by the metals and other bodies upon nitric acid is very variable. Carbon heated with strong nitric acid evolves peroxide of nitrogen N_2O_4, principally. Silver and palladium allowed to dissolve in the hydrate of nitric acid, without any application of heat, liberate nitrous anhydride N_2O_3, or the corresponding acid HNO_2, which remains in solution. The compound N_2O_3, is also produced when arsenious anhydride is dissolved in nitric acid. Copper and mercury when attacked by nitric acid evolve nitric oxide N_2O_2, most freely; whereas zinc and tin dissolve in the cold dilute acid, with production of nitrous oxide N_2O. Free nitrogen N_2, also occurs among the products of the violent action of nitric acid upon several of the metals. Thus when copper is dissolved in moderately strong nitric acid at an increased temperature, the evolved nitric oxide gas is contaminated with nitrogen; whereas when it is dissolved in weak acid, at a low temperature, the gas is contaminated with nitrous oxide. Moreover, zinc, tin, iron, and several other metals, effect a partial hydrogenation of the dilute acid into ammonia: —

$$9HNO_3 + Zn_8 = 8ZnNO_3 + 3H_2O + H_3N.$$

Nitric acid converts arsenites into arsenates, ferrous into ferric, and stannous into stannic salts. In the concentrated state, it rapidly oxidises sulphurous into sulphuric acid, and sulphydric acid into water and sulphur; but this action of weak nitric acid, when free from nitrous acid, is very gradual. Iodhydric acid and the iodides are decomposed by nitric acid, with liberation of iodine and nitric oxide: $3HI + HNO_3 = 2H_2O + I_3 + NO$. The mutual decomposition of nitric and chlorhydric acids has been described, as has also the reaction of nitric acid with nitric oxide. The action exerted by nitric acid upon organic or carbon-compounds consists principally in oxidation, and in the formation of nitro-derivatives. Indigo C_8H_5NO, for example, is oxidated into isatin $C_8H_5NO_2$, by treatment with weak nitric acid; while the strong acid converts benzene C_6H_6, into nitrobenzene $C_6H_5(NO_2)$, or into dinitrobenzene $C_6H_4(NO_2)_2$. Nitric acid often acts very violently upon organic substances. The addition of strong nitric acid to carbolic acid C_6H_6O, for instance, produces a considerable explosion, sometimes accompanied with deflagration; and warm turpentine

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$C_{10}H_{16}$ is readily inflamed by a mixture of nitric and sulphuric acids.

The liquid known as *fuming nitric acid* is a solution of pernitric oxide in the strongest nitric acid. It is made commercially by heating an excess of nitre with sulphuric acid. It has a yellowish-red colour, and fumes strongly on exposure to air. When gently heated, it yields a distillate consisting of a layer of pernitric oxide covered by a layer of coloured nitric acid. When diluted with water, it becomes successively green, blue, and colourless, with evolution of nitric oxide gas. The brown fuming acid is a much more powerful and ready oxygenant than pure nitric acid of the same degree of concentration.

(284) NITRATES. *Sym.* MNO_3.—*a.* Nitrate of sodium, better known as cubic nitre, exists in distinct layers or beds underneath the superficial soil in many parts of Chili and Peru. Nitrate of potassium, or prismatic nitre, occurs as an efflorescence from the surface of the soil in various provinces of the East Indies, particularly in the district of Tirhût, in Bengal. Nitrate of calcium is produced artificially in several countries of Europe, by mixing decomposing vegetable and animal matter with cinders, chalk, marl, &c., moistening the porous masses repeatedly with urine, exposing them freely to the air for two or three years, and lixiviating. A similar formation of nitrates results in the so-called *saltpetre-rot*, or efflorescence which sometimes occurs upon the old walls of stables and other badly-drained buildings in this country. Nitrates are produced whenever nitrogenised organic matters, in contact with earthy carbonates or other bases, are freely acted upon by the air. Lumps of chalk, moistened with weak ammonia also, and exposed to the air, have been found to yield nitrate of calcium; but it is doubtful whether the production of ammonia is a necessary stage in the process of nitrification. The shallow well-waters of towns nearly always contain nitrates from contamination with sewer or cesspool drainage, &c. But many natural waters, obtained from strata containing very little organic matter, have also proved to be charged with nitrates. Hence some chemists have inferred that these salts might be produced directly from the free nitrogen and oxygen gases dissolved in water,—the porous beds through which it filters serving to effect the combination by an action resembling that of spongy platinum. It must be borne in mind, however, that rain water always contains carbonate and nitrate of ammonium, and that these ammoniacal salts may be the real sources of the nitrates found in the waters. Nitrates are found in the

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juices of plants, particularly in those with large fleshy tuberose roots, and are probably acquired from the soil by direct imbibition. β. The nitrates of sodium and potassium are obtained by frequently recrystallising the native salts. Nitrate of potassium is, moreover, procured by decomposing crude nitrate of calcium solution with wood-ashes, crystallising by evaporation, and purifying by recrystallisation; also by decomposing nitrate of sodium with chloride of potassium. The other nitrates are made by dissolving different metals, their hydrates, oxides, or carbonates, in aqueous nitric acid, and crystallising by evaporation.

(285) The nitrates are monobasic crystalline salts. The normal nitrates are all soluble in water; their solutions are for the most part neutral, and have a cooling saline taste. The crystallised nitrates of sodium, potassium, ammonium, strontium, barium, lead, and silver are anhydrous; that of mercurosum, monhydrated; those of cadmium, calcium, and probably strontium, bihydrated; and those of magnesium, zinc, cobalt, nickel, iron, manganese, copper, and uranyl, trihydrated. Copper also forms a sesquihydrated salt $2CuNO_3.3H_2O$, corresponding to the hydrate of nitric acid. The sesquinitrate of iron crystallises with six and nine atoms of water; and ternitrate of bismuth with five atoms (Gladstone). Basic nitrate of copper has the formula $CuNO_3.3CuHO_2$, corresponding to the terhydrated salt. Most other well-defined basic nitrates are reducible to the formulæ of orthonitrates (vide par. 265).

Most of the nitrates fuse readily, and all, when strongly heated, undergo decomposition. The salts of the highly basylous metals at first give off nearly pure oxygen, with conversion into nitrites, and afterwards a mixture of oxygen and nitrogen gases, generally contaminated with some peroxide of nitrogen. Other nitrates, which are decomposed at a lower temperature, those of mercury, lead, and silver, for instance, evolve a mixture of pernitric oxide and oxygen. A few still more easily decomposible hydrated salts, the sesquinitrate of aluminium and ternitrate of bismuth, for instance, evolve unaltered nitric acid. Ignited nitrate of silver leaves a residue of metal, but most protonitrates, when strongly heated, leave residues of protoxide; those of manganese and iron, however, leave sesquioxides, or $\frac{2}{1}$-oxides. Nitrates, when heated with combustible bodies, produce a more or less violent deflagration or explosion. The acid-forming bodies, metallic and non-metallic, when deflagrated with nitre, leave sodium or potassium salts of their respective acids. All nitrates are decomposed by sulphuric and many other acids, with liberation of nitric acid, the fumes of which pro-

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duce a purple discoloration on starch-paper moistened with iodide of potassium solution. Sulphuric acid, to which a fragment of any nitrate has been added, acquires the property of bleaching indigo but not litmus, of evolving red fumes with copper-turnings, and of producing a brown colour with sulphate of iron. This last very delicate reaction is best performed by pouring a weak solution of sulphate of iron upon the mixed sulphuric acid and nitrate, so as to float thereon, whereby a deep brown halo is produced at the junction of the two liquids. The nitrates are decomposed by excess of chlorhydric acid, with formation of *aqua-regia*. Hence chlorhydric acid, to which a fragment of any nitrate has been added, acquires the property of dissolving gold leaf, and of bleaching both indigo and litmus.

Compounds of Nitrogen and Sulphur.

(286) The ammoniacal salts of the principal acids of sulphur have been already described. The remaining compounds, containing both nitrogen and sulphur, may be classified into those which are related to ammonia, and those which are related to nitric oxide or nitrous anhydride. The former class includes thionamide, thionamic acid, sulphamide, and sulphamic acid; the latter, bisulphide of nitrogen, the nitrosulphates of Pelouze, the sulphazotised salts of Fremy, and the sulphates of azotyl.

(287) Thionamide. *Sym.* N_2H_4SO; *p. n.* 80. — Precisely as sulphurous chloraldehyd may be regarded as a derivative of the double molecule of chlorhydric acid, and sulphurous acid as a derivative of the double molecule of water, in each of which double molecules two atoms of hydrogen have been displaced by one atom of the biequivalent radicle *thionyl*, so may this compound be regarded as a derivative of the double molecule of ammonia, in which two atoms of hydrogen have also been displaced by one atom of the same radicle, thus:—

H_2Cl_2	H_4O_2	H_6N_2,
$(SO)''Cl_2$	$(SO)''H_2O_2$	$(SO)''H_4N_2$.

It results from the reaction of chlorosulphurous aldehyd upon dry ammonia, according to the equation,

$$4NH_3 + SOCl_2 = 2NH_4Cl + N_2H_4SO.$$

The chlorosulphurous aldehyd should be well cooled, and the ammonia-gas passed in slowly. The product of the action is a white, pulverulent, non-crystalline solid, from which the chloride of

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ammonium may be partly extracted by means of cold water. By treatment with hot water, thionamide is converted into normal sulphite of ammonium, from which it differs in composition by the want of two atoms of water: —

$$(NH_4)_2SO_3 - 2H_2O = N_2H_4SO.$$

It is decomposed instantly by alkalis, with evolution of ammonia, and by acids, with evolution of sulphurous anhydride.

(288) THIONAMIC ACID. *Sym.* NH_3SO_2; *p. n.* 81.—This acid may be looked upon as a derivative of the single molecule of water, in which one of the hydrogen atoms has been displaced by one atom of the compound ammonium $NH_2(SO)''$, thus: $\left.\begin{matrix}NH_2(SO)''\\H\end{matrix}\right\}O$. By causing dry ammonia to react upon an excess of sulphurous anhydride, this acid is obtained as a crystalline, volatile substance, of a yellowish colour (probably accidental), and great solubility in water. In the moist state, or in solution, it speedily undergoes a complex decomposition into sulphate of ammonium, trithionate of ammonium, and other products. When sulphurous anhydride is allowed to react upon an excess of dry ammonia, two volumes of the former combine with four volumes of the latter, to form thionamate of ammonium $(NH_3)_2SO_2$, or $\left.\begin{matrix}NH_2(SO)''\\NH_4\end{matrix}\right\}O$. This is an amorphous, volatile, neutral, deliquescent salt, the solution of which undergoes speedy decomposition. Thionamic acid differs in composition from acid sulphite of ammonium by the want of one atom of water: —

$$NH_4HSO_3 - H_2O = NH_3SO_2.$$

(289) SULPHAMIDE. *Sym.* $N_2H_4SO_2$; *p. n.* 96.—This compound bears to chlorosulphuric aldehyd and sulphuric acid, the same relations that thionamide bears to chlorosulphurous aldehyd and sulphurous acid respectively. It may be looked upon as a derivative of the double atom of ammonia, in which two atoms of hydrogen have been displaced by one atom of the biequivalent radicle, *sulphuryl*, thus: —

H_2Cl_2	H_4O_2	H_6N_2
$(SO_2)''Cl_2$	$(SO_2)''H_2O_2$	$(SO_2)''H_4N_2$.

It is produced by acting on sulphuric chloraldehyd with dry ammonia, according to the equation,

$$4NH_3 + SO_2Cl_2 = 2NH_4Cl + N_2H_4SO_2.$$

Sulphamide is a white, somewhat deliquescent solid, soluble in

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water and alcohol. Owing to its solubility in water, it cannot be completely purified from the chloride of ammonium, formed simultaneously with it. Solution of sulphamide is very permanent, and gives no precipitate, either with sulphate of barium, or bichloride of platinum. By prolonged boiling, however, it takes up water to form sulphate of ammonium, and then yields precipitates with both reagents. The solution is decomposed more readily, though still by no means rapidly, when boiled with moderately strong acids or alkalis. Sulphamide differs in composition from neutral sulphate of ammonium, by the want of two atoms of water:—

$$(NH_4)_2SO_4 - 2H_2O = N_2H_4SO_2$$

When gently heated, it gives off ammonia and is most likely converted into sulphimide: $N_2H_4(SO_2)'' - NH_3 = NH(SO_2)'$. This last formula should probably be doubled, whereby the compound would appear as a variety of sulphamide, in which four atoms of hydrogen are displaced by two of sulphuryl $N_2H_2(SO_2)_2''$. We can conceive the existence of a third variety of sulphamide, in which the six atoms of hydrogen in the type have been displaced by three of sulphuryl $N_2(SO_2)_3''$.

(290) SULPHAMIC ACID. *Sym.* NH_3SO_3; *p.n.* 97.— This body, the analogue of thionamic acid, may be looked upon as a derivative of the single molecule of water, in which one atom of hydrogen has been displaced by one atom of the compound ammonium $NH_2(SO_2)''$, thus, $\left.\begin{matrix}NH_2(SO_2)''\\H\end{matrix}\right\}O$. The acid is scarcely known in the isolated state, but its ammonium salt, $\left.\begin{matrix}NH_2(SO_2)''\\NH_4\end{matrix}\right\}O$, or $(NH_3)_2SO_3$, is a very well-defined compound. Sulphamate of ammonium results from the absorption of dry ammonia by sulphuric anhydride, kept cool by means of ice. The product of the action is dissolved carefully in ice-cold water, any free sulphuric acid removed by carbonate of barium, and the filtered solution concentrated by evaporation in vacuo over oil of vitriol, when the salt crystallises out in colourless transparent hemihedral forms, of the square prismatic system. The solution of these crystals is quite neutral, and gives no precipitate with chloride of barium. With acid bichloride of platinum, one-half only of the nitrogen of the compound is precipitated in the state of double chloride of platinum and ammonium. When boiled for a long time, the salt takes up water, and is converted into a mixture of neutral sulphate, and, owing to the volatilization of ammonia, acid sulphate of ammonium. Moistened sulphamate of ammonium, by exposure to

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air, evolves ammonia and acquires an acid reaction. The solution then yields by evaporation, not only the above-described crystals of sulphamate of ammonium, but also a second crop of deliquescent prismatic needles, which, according to Laurent, constitute a hydrated double salt of sulphamic acid and sulphamate of ammonium $NH_3SO_3.(NH_3)_2SO_3.Aq$. Jacquelain obtained the same double compound in the anhydrous state, by passing the vapour of sulphuric anhydride into dry ammoniacal gas, and fusing the product in an atmosphere of ammonia. The solution of this body, though possessing an acid reaction, does not give any precipitate with chloride of barium.* Sulphamic acid may be looked upon as hydrated sulphimide $NHSO_2 + H_2O$, or as dehydrated acid sulphate of ammonium $NH_4HSO_4 - H_2O$ (vide par. 222).

(291) BISULPHIDE OF NITROGEN. *Sym.* N_2S_2, *p.n.* 92.—This compound, which has been carefully examined by Fordos and Gelis, may be regarded as a sulphur-derivative of nitric oxide. It is made by passing ammoniacal gas through a solution of protosulphide of chlorine in bisulphide of carbon. Sal-ammoniac is first deposited, and then a dark brown flaky substance, which the further action of the ammonia decomposes. The gas must be transmitted until the brown flakes have almost disappeared, and an orange-yellow liquid is formed, which may be separated from the chloride of ammonium by filtration, and obtained quite clear. The filtrate, by spontaneous evaporation, at first deposits sulphur, and afterwards bisulphide of nitrogen, in the form of transparent, golden-yellow, rhombic prisms, with dihedral summits. The final reaction may be expressed by the following equation, but many intermediate products are actually produced:—

$$3Cl_2S + 8NH_3 = N_2S_2 + S + 6NH_4Cl.$$

Sulphide of nitrogen explodes by percussion, or when heated to 150°—160°. It combines with the sulphides of chlorine in several proportions. It is insoluble in water, very sparingly soluble in alcohol, ether, and turpentine. Its solution in bisulphide of carbon undergoes a gradual decomposition.

(292) NITRO-SULPHATES.—These salts are usually regarded as sulphates, in which one atom of diequivalent oxygen has been displaced by two atoms of protequivalent azotyl, thus, $K_2SO_3(NO)_2$.

* Jacquelain's compound $(NH_3)_2SO_3$, might also be formulated on the type of the double molecule of water, thus: $-N_2H_4(SO_2)_2''\}O_2$.
$NH_4.H\ \}$

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A dry mixture of two volumes of sulphurous anhydride and four of nitric oxide, though of itself permanent, is gradually absorbed by a strong solution of caustic potash or soda, with formation of a nitrosulphate of alkali-metal. Nitrosulphate of ammonium is prepared by passing a current of nitric oxide gas, for some hours, through a cooled mixture of one measure of concentrated solution of sulphite of ammonium with five or six measures of aqueous ammonia. Beautiful white crystals gradually form, which are to be washed with an ice-cold solution of ammonia, dried in vacuo, and preserved in a well-closed bottle. The potassium and sodium salts are procurable in a similar manner. They are rather more stable than the ammonium salt.

Nitrosulphate solutions have a sharp, bitter taste, are neutral to test paper, and do not give any precipitate with chloride of barium. They are permanent only at the freezing point, or in presence of an excess of caustic alkali. Their spontaneous decomposition into nitrous oxide and a sulphate varies in its rapidity according to the temperature. Free acids and most metallic salts transform the nitrosulphates immediately into sulphuric acid and nitrous oxide gas. A similar decomposition of the salts is effected by contact with spongy platinum, charcoal, oxide of silver, peroxide of manganese, &c.:—

$$K_2SO_3(NO)_2 = K_2SO_4 + N_2O.$$

Dry nitrosulphate of ammonium is decomposed with almost explosive violence when heated to a temperature but little above that of boiling water.

(293) SULPHAZOTISED SALTS.—Fremy has described a very interesting series of salts, procured for the most part by the action of sulphurous acid upon nitrite of potassium dissolved in excess of alkali. The compounds resulting from different modifications of the process have very different compositions, but, at present, their formulæ cannot be looked upon as satisfactorily determined. The best defined class of these salts is that of the sulphammonates, which may be regarded as derivatives of the quadruple molecule of sulphurous acid, in which one atom of hydrogen has been displaced by one of nitric oxide, and four atoms of hydrogen by four of metal, thus:—

$H_7NO(SO_3)_4$ Sulphammonic acid.
$K_4H_3NO(SO_3)_4$ Sulphammonate of potassium.
$Ba_3KH_3NO(SO_3)_4$ Sulphammonate of barium and potassium.
$(NH_4)_4H_3NO(SO_3)_4$ Sulphammonate of ammonium.
$Ba_3(NH_4)\ H_3NO(SO_3)_4$ Sulphammonate of barium and ammonium.

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Sulphammonate of potassium * may be formed by mixing solutions of nitrite and sulphite of potassium, or by passing a rapid current of sulphurous acid into a not too concentrated solution of nitrite of potassium. It occurs as an abundant white crystalline deposit, scarcely soluble in cold, moderately soluble in warm water, from which it crystallizes out on cooling in brilliant needles. Its solution is insipid, and without action on vegetable colours. When boiled for a few minutes it is decomposed, with disengagement of sulphurous acid, and formation of an acid liquid, containing a mixture of neutral and acid sulphates of potassium and ammonium. The ammonium resembles the potassium salt, save that it is somewhat more soluble. The double barium salts are made by adding chloride of barium to the warm solution of the potassium salt, or to the cold solution of the ammonium salt. Silicofluorhydric acid liberates a very unstable sulphammonic acid from the sulphammonate of potassium. All sulphazotised salts, including the sulphammonates, are more or less unstable, but manifest a certain degree of permanence in the presence of free alkali. No sulphazotised salts of sodium, and with the exception of the sulphammonates, no sulphazotised salts of ammonium have been obtained.

(294) SULPHATES OF AZOTYL.—These compounds may be compared with the corresponding salts of sodium, thus:—

$HNaSO_4$	Acid sulphate	$H(NO)SO_4$
Na_2SO_4	Neutral sulphate	$(NO)_2SO_4$
$Na_2S_2O_7$	Anhydro-sulphate	$(NO)_2S_2O_7$

It will be remembered that acid sulphate of sodium is converted into anhydro-sulphate by the action of heat, and anhydro-sulphate into acid-sulphate by treatment with water:—

$$2NaHSO_4 - H_2O = Na_2S_2O_7.$$

Acid sulphate of azotyl was obtained by Weltzien as a white crystalline mass, by passing nitrous anhydride into normal sulphuric acid:—

$$2H_2SO_4 + (NO)_2O = 2(NO)HSO_4 + H_2O.$$

It is probably identical with the compound formed by dissolving

* Fremy's formula for this salt, $4K_2O.3H_2O.N_2O_3.8SO_2$, may obviously be translated into that above given, which is somewhat simpler though equally empirical. The per-centage composition of the salt is not absolutely established, but seems to accord very well with Fremy's expression.

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the anhydro-sulphate in sulphuric acid containing a little water, and crystallising:—

$$(NO)_2S_2O_7 + H_2O = 2(NO)HSO_4.$$

Neutral sulphate of azotyl has been described by Gay Lussac, Provostaye, Mitscherlich, and others. It results from the reaction of pernitric oxide upon sulphuric acid, thus:—

$$H_2SO_4 + 4NO_2 = (NO)_2SO_4 + 2HNO_3.$$

By this process, Gay Lussac obtained the compound crystallised in four-sided prisms. It is, moreover, procurable in many other ways.

The anhydro-sulphate is formed by the action of sulphurous anhydride upon pernitric oxide (Provostaye), and of sulphuric anhydride upon nitric oxide (Brüning), according to the following equations:—

$$2SO_2 + 4NO_2 = (NO)_2S_2O_7 + N_2O_3.$$

$$3SO_3 + 2NO = (NO)_2S_2O_7 + SO_2.$$

It occurs as a hard, white, amorphous mass, which fuses when heated, and is volatile without decomposition. It dissolves in concentrated oil of vitriol, apparently without change; but with a slightly diluted sulphuric acid, it forms a bulky crystalline substance, probably identical with Weltzien's body. All the sulphates of azotyl are deliquescent, and immediately decomposed by excess of water into sulphuric acid and nitric oxide gas. During the manufacture of oil of vitriol, when an insufficient quantity of steam is admitted into the chambers, a crystalline deposit is formed, consisting of some or other of the sulphates of azotyl.

§ II. Phosphorus.

Symbol P; *Proportional Number*, 31; *Vapour-density*, 15·5; *Atomic Volume* □.

(295) Phosphorus occurs in nature, almost always in the state of a metallic phosphate, and chiefly as phosphate of calcium, which forms the principal constituent of the well-known minerals apatite, phosphorite, coprolite, &c. Combined phosphoric acid is also found, though in very minute proportions, in most of the primitive rocks, and in soils produced by their disintegration; whence it is taken up by plants, in the seeds of which it becomes principally accumulated. From the vegetable it passes into the animal kingdom, where it exists in the largest proportion. It is found in the blood, in the urine, in all the soft tissues, especially

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the nervous tissue, and in the bones, of which indeed phosphate of calcium forms the principal earthy constituent. Brandt, of Hamburg, in 1669, discovered phosphorus, which he extracted from human urine. Gahn, in 1768, pointed out the relation of phosphoric acid to bone-earth, which was soon afterwards employed as a source of phosphorus by Scheele, and by Fourcroy and Vauquelin.

(296) Earthy and alkaline phosphates, with three atoms of metal, bone-earth, for instance, Ca_3PO_4, are not decomposed by ignition with charcoal; but phosphoric acid and anhydride are completely reduced, while the metaphosphates, which may be regarded as compounds of trimetallic phosphate with phosphoric anhydride, are partially reduced. Two-thirds of the phosphorus existing in metaphosphate of calcium, for instance, are set free by ignition with charcoal, while one-third is left in the form of bone-earth, thus: $3CaPO_3 = P_2O_5$, which is reduced, + Ca_3PO_4, which remains. Hence the first stage in the manufacture of phosphorus consists in the production of metaphosphate of calcium.

Bones are burnt to a white ash, which is finely powdered, and mixed with a sufficient quantity of dilute sulphuric acid to abstract two-thirds of the calcium from the triphosphate of calcium, and to decompose the whole of the carbonate of calcium existing in the bone-ash. About 3 parts of bone-ash and 2 of sulphuric acid, mixed with 18 of water, are the proportions usually employed:—

$$Ca_3PO_4 + H_2SO_4 + 2H_2O = CaH_2PO_4 + Ca_2SO_4 . 2H_2O.$$

After subsidence, the soluble monocalcic phosphate is strained and pressed from the insoluble gypsum, which is slightly washed with water. The washings are added to the phosphate solution, which is then evaporated to a syrupy consistency, mixed with about $\frac{1}{4}$ of its weight of fine charcoal, and heated gradually to dull redness in an iron-pot, stirring all the time. By this means a porous mixture of charcoal and metaphosphate of calcium is obtained: $CaH_2PO_4 = CaPO_3 + H_2O$. This is introduced into an earthern retort, covered with a paste of clay and borax, to render it less porous, and submitted to the action of a full red heat, whereby the phosphorus is separated and driven off in vapour:—

$$3CaPO_3 + C_5 = Ca_3PO_4 + 5CO + P_2.$$

By mixing sand with the charcoal paste, as recommended by Wöhler, the whole of the phosphorus may be expelled, thus:—

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$$4CaPO_3 + 2SiO_2 + C_{10} = 2Ca_2SiO_3 + 10CO + P_4.$$

The phosphorus vapour is conveyed from the retort, by means of a bent copper tube, into a closed vessel of water, wherein it becomes condensed as a reddish yellow deposit, while the uncondensable gases escape from the receiver through an exit pipe leading to a flue. The phosphorus is purified by fusion under water, filtration through wash-leather, and successive treatment with ammonia and bichromate of potassium dissolved in dilute sulphuric acid. It is sometimes further purified by distillation in an atmosphere of hydrogen or nitrogen. The melted phosphorus is ordinarily drawn or cast into cylindrical moulds, within which it solidifies to form stick phosphorus.

(297) Ordinary phosphorus, when pure, is either colourless or of a very pale lemon-yellow tint; but commercial phosphorus has often a deep orange colour, resulting from its exposure to light. It is usually transparent, but after rapid cooling from the melted state acquires a semi-opaque and crystalline aspect. It has even been obtained in definite octahedral and dodecahedral crystals by the way of fusion; and is readily procured in one or other of these forms by the slow evaporation of its solution in bisulphide of carbon, or other menstruum. Ordinary phosphorus has a specific gravity 1·82—1·84. It has a waxy consistency at common temperatures, but becomes brittle at zero. It is a non-conductor of electricity, whether in the solid or liquid state. It fuses at 44°—5°, with considerable expansion, into a transparent highly refractive oil, which often remains for a long time liquid, at temperatures greatly below the melting point of the solid element. This phenomenon is especially manifested when phosphorus is melted under a solution of caustic potash. But on touching the melted substance with a wire or glass rod, it instantly solidifies, and experiences an obvious rise in temperature. Phosphorus boils at 290°, yielding a colourless gas, of which the density is 62 times that of hydrogen at the same temperature. Consequently, an atom of phosphorus vapour occupies only half the volume of an atom of hydrogen gas; and this relation is maintained up to 1000°, the highest temperature at which the examination has been made (Deville). Phosphorus volatilises slowly at ordinary temperatures, and readily in the vapour of boiling water.

Phosphorus is quite insoluble in water, and almost insoluble in alcohol. It dissolves, to a small extent, in ether, and in the fixed

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and volatile oils. It is somewhat more soluble in benzene and rock-oil, while it dissolves readily in bisulphide of carbon, subchloride of sulphur, and trichloride of phosphorus. Phosphorus is extremely inflammable, and takes fire when heated in the open air, to a temperature but very little above its melting point, burning with a highly luminous flame, and evolving an opaque white smoke of phosphoric anhydride. It is also readily inflamed by friction, and on account of its easy inflammability, is usually kept under water. When exposed to the air, at all temperatures above zero, it undergoes a slow combustion, and in the dark emits a pale bluish light, whence its name (*φῶς φορὸς*). Finely divided phosphorus, produced, for instance, by moistening a piece of filtering paper with the solution of phosphorus in bisulphide of carbon, and allowing the solvent to evaporate, bursts into flame spontaneously. Spontaneous combustion will often take place also when several small pieces of phosphorus are wrapped in cotton wool, so as to prevent external cooling. The slow combustion of phosphorus is attended with the production of a peculiar garlic odour, and an evolution of white fumes of phosphorous acid or anhydride. According to Graham, the slow combustion, and consequent luminosity of phosphorus, is prevented by the presence in air of very minute traces of certain inflammable gases and vapours, olefiant gas, ether, naphtha, and turpentine, for instance. Moreover, the luminosity of phosphorus is not manifested in pure oxygen at temperatures below 15°; but is readily produced by rarefying the gas considerably, or by mixing it with hydrogen, nitrogen, or carbonic acid. Rarefaction also overcomes the action of the above-mentioned gases and vapours in checking the luminosity of phosphorus in air.

Phosphoric anhydride is the principal product of the rapid burning of phosphorus, while phosphorous acid results from its slow combustion. Phosphorus is also readily converted into phosphorous and phosphoric acids by treatment with nitric acid and other oxidising agents. At a gentle heat, it combines somewhat violently with sulphur to form definite sulphides of phosphorus. Its union with chlorine, bromine, and iodine takes place spontaneously, and is usually attended with combustion. When phosphorus is boiled in solution of caustic alkali, it yields a hypophosphite and evolves phosphoretted hydrogen gas. It very slowly effects a similar decomposition of water into hypophosphorous acid and phosphoretted hydrogen. It is a powerful reducing agent, and causes metallic deposits with greater or less

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facility, in solutions of gold, platinum, palladium, silver, mercury, and copper respectively. At elevated temperatures, most of the metals combine with phosphorus to produce metallic phosphides; which are also formed by the action of phosphorus upon heated metallic oxides.

(298) Phosphorus, like sulphur, is remarkable for its capability of existing in several allotropic forms. Colourless transparent phosphorus preserved under water, and exposed to ordinary daylight, becomes superficially changed into an opaque white friable modification of the element. This alteration seems to consist in a spontaneous subdivision of the phosphorus into an aggregation of small plates, which present a semi-crystalline appearance. The sp. gr. of white phosphorus is 1·5. It is reconverted into the ordinary variety at a temperature of 50° and upwards. When ordinary phosphorus is heated to some degrees above its melting point, and suddenly cooled, it is instantly changed into an opaque black mass; which, however, on being remelted, and then slowly cooled, re-acquires its usual appearance. But when phosphorus is heated nearly to its boiling point and suddenly cooled, it assumes a peculiar viscous condition, resembling that of viscous sulphur.

The most extraordinary modification of phosphorus, however, is that which is generally known as amorphous phosphorus. When common phosphorus is exposed to direct sunlight, or to a high temperature, either in vacuo, or in an inactive gas, it gradually assumes a red colour, and becomes greatly changed in its properties. This form of phosphorus may be procured on a large scale by Schrötter's process, which consists in heating ordinary phosphorus for some hours to a temperature of 230 — 50°, in a flask or retort filled with nitrogen or carbonic anhydride, and having its beak dipping into a vessel of mercury. A small quantity of ordinary phosphorus is driven over unchanged, but the chief portion is converted in great measure into the amorphous variety; which may be purified from any admixture with ordinary phosphorus by treatment with bisulphide of carbon, in which the red modification is quite insoluble. Amorphous phosphorus usually occurs as a chocolate red powder, but in specimens prepared at a somewhat high temperature the colour is vermilion red. Its sp. gr. is 2·14 (Brodie). It melts at 250° — 60°, with reconversion into ordinary phosphorus. It is devoid of taste and smell. At ordinary temperatures, it may be exposed freely to the air without undergoing any appreciable alteration. It does not become luminous until heated to 200°, or inflame

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below 260°. It is readily acted upon by chlorine, but does not take fire therewith. It is insoluble in bisulphide of carbon, rock-oil, and terchloride of phosphorus. It is not poisonous. Amorphous phosphorus may be obtained in a more compact state by keeping common phosphorus for several days at a temperature but little below 260°. It then constitutes a reddish-brown mass, having a lustrous conchoidal fracture, and yielding a chocolate red powder.

Brodie has shown that a small quantity of iodine can convert an almost indefinitely large quantity of phosphorus into the amorphous condition. For this experiment the phosphorus may be melted in a glass flask filled with carbonic anhydride. Then, on projecting the iodine through an upright tube reaching nearly to the phosphorus, and gently warming, a violent action takes place, attended with the development of intense heat. The product of the experiment constitutes a very hard, semi-metallic, black mass, giving a red powder. The same result may be obtained by adding the iodine to phosphorus melted under chlorhydric acid. Amorphous phosphorus, prepared by Brodie's process, may be distilled without transformation. It volatilizes without fusing, exactly like arsenic, and condenses in the form of a hard black mass, containing a mere trace of iodine. It is more readily acted upon by caustic potash than the variety produced by Schrötter's process, and is capable of precipitating certain metallic solutions, sulphate of copper for instance. Its sp. gr. is 2·23. In Brodie's process, an iodide of phosphorus is first formed, the combined phosphorus of which exists in the amorphous state. This compound is then decomposed, with separation of its amorphous phosphorus, and formation of a more volatile iodine-product, which reacts upon a second portion of phosphorus to re-form the first decomposible iodide, and so on, continuously. By performing the experiment in a long combustion tube, the consecutive conversion can be traced from one end of the tube to the other. By reason of this mode of formation, amorphous phosphorus would seem to constitute the electro-positive variety of the element, corresponding to the amorphous sulphur produced by the decomposition of chloride of sulphur.

Phosphoretted Hydrogen, or Phosphamine.

Symbol, H_3P; *Proportional number*, 34; *Vapour-density*, 17; *Atomic volume*, □□.

(299) Phosphoretted hydrogen gas is produced by the spontaneous decomposition of phosphorised organic bodies, decaying

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fish, for example. Its natural evolution appears to be the cause of *ignes fatui* and similar luminous appearances. Phosphoretted hydrogen, though liberated in many chemical reactions, is scarcely procurable in a state of purity. It is almost always mixed with a greater or less proportion of free hydrogen, and is frequently contaminated with the vapour of a liquid phosphide of hydrogen H_2P, or H_4P_2, which gives to it the property of spontaneous inflammability. The spontaneously inflammable gas was discovered in 1783 by Gengembre, and the non-spontaneously inflammable variety some years afterwards by Davy.

a. The non-spontaneously inflammable gas is produced by deoxidating solutions of hypophosphorous and phosphorous acids with zinc and sulphuric acid, or by acting upon phosphoric acid with potassium or sodium.

β. Hypophosphorous and phosphorous acids, when heated, break up into phosphoric acid and non-spontaneously inflammable phosphoretted hydrogen, which may be collected over water :—

Hypophosphorous $2H_3PO_2 = H_3P + H_3PO_4$.

Phosphorous $4H_3PO_3 = H_3P + 3H_3PO_4$.

According to Dumas and Rose, the first portions of gas evolved by this process are pure, but the later portions contain a considerable quantity of hydrogen. The phosphorous acid should be heated gently in a flask of hard glass, to prevent the formation of any phosphite of alkali-metal, which in its decomposition would yield free hydrogen. By the application of a stronger heat, not only hypophosphorous acid, but also the hypophosphites yield phosphoretted hydrogen; which, however, when produced from the salts, is usually spontaneously inflammable and mixed with hydrogen.

γ. Under the influence of sunlight, phosphoretted hydrogen in small quantity, together with suboxide of phosphorus (?), is produced by the reaction of finely divided phosphorus upon water. But when phosphorus is boiled with water and a fixed alkali, spontaneously inflammable phosphoretted hydrogen gas is readily produced. The hydrates of sodium, potassium, calcium, strontium and barium effect the reaction, and according to some authors, those of magnesium, zinc, and iron (ferrosum) also. Phosphoretted hydrogen and a hypophosphite are the principal products obtained with the alkaline earths :—

$$3CaHO + P_4 + 3H_2O = 3CaH_2PO_2 + H_3P.$$

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But with the true alkalies, there is a large amount of free hydrogen and phosphate of alkali-metal formed in addition, owing to the decomposition which hypophosphites undergo when boiled in strongly alkaline liquids. In making phosphoretted hydrogen by heating phosphorus with milk of lime or solution of caustic potash, it is necessary, in order to avoid explosions, that the retort or flask in which the reaction is effected should not contain much air or oxygen. The air may be swept out by vaporizing a little ether from the surface of the liquid, or preferably by passing a current of hydrogen or nitrogen gas through the apparatus.

δ. Phosphoretted hydrogen gas may be produced by acting with water or acid upon certain impure phosphides, obtained by heating phosphorus with the alkaline earths and other bases. Phosphide of calcium, for instance, may be introduced into a small flask completely filled with dilute chlorhydric or nitric acid, and the cork, with a somewhat narrow delivery tube, then quickly inserted. The evolution of the gas, which is spontaneously inflammable, may be accelerated by the application of a gentle heat. When phosphide of calcium is thrown into water, spontaneously inflammable phosphoretted hydrogen gas is slowly liberated. The bubbles as they reach the surface take fire, burn with a highly luminous flame, and produce thick clouds of white smoke, which in a quiet atmosphere ascend in the form of successive gradually expanding rings. But phosphide of calcium when decomposed by concentrated chlorhydric acid, yields the non-spontaneously inflammable gas. Dumas wraps the phosphide of calcium in paper, and passes the package up into strong chlorhydric acid standing over mercury. The decomposition is almost instantaneous, and the resulting gas very nearly pure.

Spontaneously inflammable phosphoretted hydrogen may be freed from the compound PH_2, by passing it through a freezing mixture of ice and salt; but according to Graham, the addition of a minute quantity of nitric oxide gas will again confer on it the property of spontaneous inflammability. It is also rendered non-spontaneously inflammable by exposure to sunlight, by contact with charcoal and other pulverulent bodies, and by admixture with the vapours of chlorhydric acid, ether, alcohol, turpentine, &c. (vide pars. 302 and 303).

(300) Phosphoretted hydrogen is a colourless condensable gas, having a very offensive garlic-like smell. It is sparingly soluble in water, more so in alcohol, ether, and the volatile oils. Neither the gas nor its solutions have any action upon blue or red litmus-

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paper. By the transmission of a series of electric sparks, two volumes of phosphoretted hydrogen are converted, with deposition of phosphorus, into three volumes of hydrogen. Most of the metals, when heated in the gas, combine with its phosphorus and liberate its hydrogen. A mixture of the non-spontaneously inflammable gas and oxygen, standing over water, is gradually absorbed with production of phosphorous acid. The mixture of the two gases, though changed very gradually at ordinary pressures, undergoes when suddenly rarified, an instantaneous decomposition, attended with a violent explosion. Phosphoretted hydrogen is readily inflammable, burning with a brilliant flame, and evolving a white smoke of phosphoric acid. The gas not only combines with free oxygen, but effects a speedy reduction of very many oxidised bodies. Thus it is decomposed by nitric oxide, nitric acid, sulphurous anhydride, and sulphuric acid, with deoxidation of the respective reagents. Pure phosphoretted hydrogen is completely absorbed by solutions of hypochlorous acid and the soluble hypochlorites.

Chlorine, bromine and iodine decompose phosphoretted hydrogen with abstraction of its hydrogen. If in excess, they also combine with its phosphorus to form the respective chlorides, bromides, and iodides, or their products of decomposition with water. When bubbles of phosphoretted hydrogen gas are introduced into a receiver of chlorine, they inflame with a sharp explosion and production of chlorhydric acid and pentachloride of phosphorus. Sulphur, heated in phosphoretted hydrogen, forms sulphuretted hydrogen and sulphide of phosphorus. Phosphoretted hydrogen precipitates the solutions of many metallic salts; those of lead very slowly, those of copper more quickly, and those of the noble metals most readily of all. The precipitates, save those produced with mercury salts, are black or dark coloured. They consist of metallic phosphide as in the case of copper, of mixed phosphide and metallic salt as in the case of mercury, or of reduced metal as in the case of silver and gold. Solution of sulphate of copper is often used for estimating the proportion of free hydrogen in ordinary phosphoretted hydrogen, by observing the quantity of gas which it leaves unabsorbed.

(301) Phosphoretted hydrogen, though devoid of any alkaline reaction, is in other respects closely analogous to ammonia. Thus it unites directly with iodhydric acid to form the iodhydrate of phosphamine PH_3HI, or iodide of phosphonium PH_4I; and a corresponding compound has been obtained with bromhydric acid.

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Moreover, like ammonia, phosphoretted hydrogen unites with the perchlorides of many metals to form white saline bodies of similar constitution to the nitrogen-compounds. Iodhydrate of phosphamine is usually made by adding a little water to equal atomic proportions of iodine ground up with powdered glass, and phosphorus cut up into small pieces. Vapours of the iodhydrate of phosphamine mixed with those of iodhydric acid are immediately evolved, the former of which condense as a crystalline deposit. But Hofmann has shown that the compound may be preferably made by gently heating iodine in a current of dry phosphoretted hydrogen gas, according to the equation,

$$I_5 + 4H_3P = PI_2 + 3H_4PI.$$

The salt crystallises in cubes, which fuse when moderately heated, and, out of access of air, may be sublimed without change. They are deliquescent, and decomposible by water into iodhydric acid and phosphamine.

Again, the radicle-derivatives of phosphoretted hydrogen correspond exactly in their properties with the similar derivatives of ammonia. Hofmann and Cahours' triethylphosphine PEt_3, for instance, is a volatile liquid which neutralizes various acids to form crystalline salts. The chlorhydrate of triethylphosphine PEt_3HCl, or representative of the chlorhydrate of triethylamine NEt_3HCl, forms with bichloride of platinum, a double salt $PEt_3HCl.PtCl_2$, corresponding to the triethylamine compound $NEt_3HCl.PtCl_2$. Iodide of ethyl unites directly with triethylphosphine to form an iodide of tetrethylphosphonium PEt_4I, corresponding to the iodide of tetrethylammonium NEt_4I. From this salt, the hydrate of tetrethylphosphonium PEt_4HO, corresponding to the hydrate of tetrethylammonium NEt_4HO, may be prepared. Like its nitrogen representative, it constitutes a non-volatile solid, which dissolves in water, forming a strongly alkaline caustic liquid, resembling a solution of caustic potash or soda.

(302) Liquid Phosphide of Hydrogen. — The spontaneous inflammability of certain varieties of phosphoretted hydrogen seems to depend, as pointed out by P. Thenard, upon the presence therein of a minute proportion of the vapour of a liquid compound, which has the constant property of taking fire by contact with oxygen, and of conferring that property, not only upon phosphamine, but upon any combustible gas with which its vapour is mixed, even in the most minute proportion. It may be pro-

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cured by conducting the spontaneously inflammable phosphoretted hydrogen, evolved by the reaction of water and phosphide of calcium, through a U-tube immersed in salt and ice. A colourless highly refrangible liquid condenses, which takes fire immediately it meets with air, and burns with the bright white light of phosphorus. It is decomposed by exposure to light, and by contact with chlorhydric acid. It remains liquid at $-20°$; it is insoluble in water, soluble in alcohol and ether. Its composition is usually expressed by the formula H_2P, but it is thought by some chemists to contain the elements of water, and to constitute the hydrogen representative of oxichloride of phosphorus, namely, H_3PO. The introduction of bubbles of spontaneously inflammable phosphoretted hydrogen into oxygen gas is attended with a succession of instantaneous flashes of brilliant light, and of sharp explosions, which not unfrequently break the receiver.

(303) Solid Phosphide of Hydrogen.—Leverrier first observed that when spontaneously inflammable phosphoretted hydrogen is exposed to sun-light, a solid yellowish compound is deposited on the sides of the glass, and simultaneously the gas loses its property of spontaneous inflammability. The same solid compound is obtainable in larger quantity by treating liquid phosphide of hydrogen with chlorhydric acid, or even by dissolving phosphide of calcium in strong chlorhydric acid, which seems to cause a decomposition of the liquid body into phosphoretted hydrogen gas and the solid phosphide. Hence spontaneously inflammable phosphoretted hydrogen, when transmitted through aqueous chlorhydric acid, becomes non-spontaneously inflammable, and yields a deposit of solid phosphide. This solid phosphide is insoluble in water and alcohol. It dissolves in warm potash, with liberation of non-spontaneously inflammable phosphoretted hydrogen. It takes fire at about 150°. Its composition is doubtful, but is usually expressed by the formula P_2H.

Phosphides.

(304) The metallic derivatives of phosphamine, represented by the general formula M_3P, constitute a comparatively unimportant class of salts, none of which are found native. Many of them are made by transmitting phosphoretted hydrogen gas over the heated metals or their oxides, or by passing the gas into solutions of their respective salts, thus:—

$$3CuCl + PH_3 = 3HCl + PCu_3.$$
$$3Cu_2Cl + PH_3 = 3HCl + PCu_6.$$

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Others are obtained by treating the metals directly with phosphorus. The phosphides of the heavy metals are, for the most part, brittle lustrous solids, which, at very high temperatures, give up a part or the whole of their phosphorus. The phosphides of the alkaline earth-metals, that of calcium for instance, are formed by passing the vapour of phosphorus over the red-hot oxides, whereby phosphides and phosphates are simultaneously produced. The products of the reaction constitute brown powders, having an opaque earthy aspect. When acted on by water or dilute acids, they evolve spontaneously inflammable phosphoretted hydrogen, leaving hypophosphites, or hypophosphorous acid, in solution.

The composition of some metallic phosphides seems to accord with the formula PM_2, corresponding to that of the diniodide of phosphorus PI_2, and to that of many native arsenides AsM_2. Metallic phosphides are, for the most part, readily oxidisable and combustible; whereby they are converted into phosphates, or mixtures of metal and phosphoric anhydride.

Halogen Compounds of Phosphorus.

(305) Trichloride of Phosphorus. *Sym.* Cl_3P; *p. n.* 137·5; *v. d.* 68·75; □□.—This compound, the chloro-derivative of phosphoretted hydrogen H_3P, and consequently the chloraldehyd of phosphorus acid H_3PO_3, is best prepared by passing a slow current of thoroughly dried chlorine through an excess of dry melted phosphorus, and distilling. It also results from passing phosphorus vapour over heated corrosive sublimate, and from the decomposition of phosphoretted hydrogen by chlorine gas. It is a colourless fuming liquid, of sp. gr. 1·45, and boiling point 74°. It dissolves phosphorus freely, and is itself soluble in benzene and in bisulphide of carbon. It absorbs chlorine readily to form the pentachloride, and, at a boiling heat, absorbs oxygen to form the oxichloride (Brodie). It is decomposed by water after the manner of chloraldehyds generally, to form chlorhydric and phosphorous acids, thus:—

$$3H_2O + Cl_3P = 3HCl + H_3PO_3.$$

(306) Pentachloride of Phosphorus. *Sym.* Cl_5P, or Cl_3PCl_2; *p. n.* 208·5; *v. d.* 52·1; ⊞.—This compound may be obtained by acting upon phosphorus, or trichloride of phosphorus, with an excess of dry chlorine. Brodie prepared it by passing dry chlorine into a solution of phosphorus in bisulphide of carbon, whereby

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it was deposited in distinct rhombic crystals. It usually occurs as a yellow crystalline mass, which volatilises below 100°, and can only be fused under pressure. It absorbs water from the atmosphere, with production of chlorhydric acid and oxichloride of phosphorus:—

$$H_2O + Cl_5P = 2HCl + Cl_3PO.$$

It is used constantly in the laboratory for preparing the chlorides of different compound radicles, especially of electro-negative radicles, for which purpose it was first employed by Cahours. Benzoic acid and pentachloride of phosphorus, for instance, produce chloride of benzoyl and oxichloride of phosphorus, which are separated by fractional distillation:—

$$C_7H_5O.HO + Cl_5P = C_7H_5O.Cl + HCl + Cl_3PO.$$

(307) Oxichloride of Phosphorus. *Sym.* Cl_3PO; *p. n.* 153·5; *v. d.* 71·75; □□. — This compound, the trichloraldehyd of phosphoric acid, is nearly always obtained as a by-product in the preparation of electro-negative chlorides, that of benzoyl, for instance, as above described. It may also be made by exposing pentachloride of phosphorus to moist air until it has nearly all liquified; by passing a current of oxygen into boiling terchloride of phosphorus; and by mixing pentachloride of phosphorus with phosphoric anhydride:—

$$P_2O_5 + 3Cl_5P = 5Cl_3PO.$$

Oxichloride of phosphorus is a colourless fuming liquid, of sp. gr. 1·7, and boiling point 110°. It is decomposed by water, after the manner of chloraldehyds generally, to form chlorhydric and phosphoric acids:—

$$3H_2O + Cl_3PO = 3HCl + H_3PO_4.$$

Like pentachloride of phosphorus, the oxichloride is largely used for preparing the chlorides of different radicles, according to a reaction first introduced by Gerhardt. Acetate of lead and oxichloride of phosphorus, for instance, form chloride of acetyl and phosphate of lead, thus:—

$$3(C_2H_3O.PbO) + Cl_3PO = 3(C_2H_3O.Cl) + Pb_3PO_4.$$

(308) Sulphochloride of Phosphorus. *Sym.* Cl_3PS; *p. n.* 169·5. — This compound, the sulphur derivative of phosphoric

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chloraldehyd, is made by decomposing pentachloride of phosphorus with sulphuretted hydrogen:—

$$H_2S + Cl_5P = 2HCl + Cl_3PS.$$

It is a heavy colourless liquid, which boils at 128°. It is scarcely decomposible by water; but, when boiled with caustic soda, forms chloride and sulphoxiphosphate of sodium (Wurtz):—

$$6HNaO + Cl_3PS = 3NaCl + Na_3PO_3S + 3H_2O.$$

Sulphoxiphosphate of sodium crystallises with twelve atoms of water in the form of brilliant six-sided tables, and is consequently heteromorphous with the corresponding normal oxisalt, $Na_3PO_4.12H_2O$. Its solution has a strongly alkaline reaction, and is immediately decomposed by chlorine, bromine, or iodine, with separation of sulphur, and formation of common phosphate of sodium. Sulphoxiphosphoric acid is liberated by the addition of almost any acid to the sodium-salt; and is decomposed by boiling. The sulphoxiphates of calcium, strontium, and barium constitute white precipitates. Those of the heavy metals decompose, either spontaneously or on the application of heat, with formation of metallic sulphides.

(309) BROMIDES OF PHOSPHORUS. — We are acquainted with a tribromide Br_3P, a pentabromide Br_5P, and an oxybromide Br_3PO, corresponding respectively to the above described chlorine compounds, which they resemble closely in their properties and modes of formation. The tribromide is a colourless liquid, which dissolves phosphorus readily. Its sp. gr. is 2·85. It boils at 175·3°, and does not solidify in a freezing mixture of salt and ice. The pentabromide is an orange-coloured, crystalline solid, which, when heated, volatilizes without fusing. By exposure to moist air, it yields the oxibromide; and by reacting with sulphuretted hydrogen, it forms a sulphobromide. The oxibromide is a dense colourless liquid, boiling at 170°—200°. It is slowly decomposed by water, with formation of bromhydric and phosphoric acids.

(310) IODIDES OF PHOSPHORUS. — There is a teriodide I_3P, corresponding to the trichloride and tribromide, and a diniodide I_2P, of which there is no chlorine or bromine representative. These iodides are prepared by dissolving phosphorus and iodine together in bisulphide of carbon, and cooling the liquid artificially until crystals are deposited. The two elements should be dissolved in atomic proportions, but when other proportions are used, the

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same compounds crystallise out, mixed with excess of either phosphorus or iodine.

The dinodide I_2P, melts at 110°, forming a red liquid which condenses into a light red solid. It is soluble in bisulphide of carbon, and is deposited therefrom in flattened prismatic orange-coloured crystals. It is decomposed by water into iodhydric and phosphorous acids, and a deposit of yellow flakes. This iodide seems to constitute the bright red compound, formed by dissolving a small quantity of iodine in melted phosphorus and heating the mixture to about 125° (Brodie).

The teriodide I_3P, fuses at 55°, and on cooling crystallises in well-defined prisms. It is very soluble in bisulphide of carbon, and is deposited therefrom in hexagonal laminæ of a dark red colour. It absorbs moisture from the atmosphere, forming iodhydric and phosphorous acids.

Oxidised Compounds of Phosphorus.

(311) By analogy, phosphoretted hydrogen should yield the following series of oxides:—

H_3P	Phosphorous aldehyd.
H_3PO	Phosphoric aldehyd.
H_3PO_2	Hypophosphorous acid.
H_3PO_3	Phosphorous acid.
H_3PO_4	Phosphoric acid.

The three acids are well-defined bodies, obtainable by various processes; but phosphoric aldehyd has not hitherto been produced. We are, however, acquainted with its chloro-representative Cl_3PO, and its ethyl representative Et_3PO.

The relations of the three acids to one another and to phosphoretted hydrogen are very instructive. Hypophosphorous acid H_3PO_2, has not been obtained directly from phosphoretted hydrogen H_3P; but, on the other hand, phosphoretted hydrogen results from the deoxidation of hypophosphorous acid, as when, for example, zinc is dissolved in the aqueous acid, either alone or mixed with sulphuric acid. Solution of hypophosphorous acid, when exposed to the air, becomes gradually converted into phosphorous acid, and finally into phosphoric acid. When heated by itself, hypophosphorous acid is decomposed into phosphoric acid and phosphoretted hydrogen: $2H_3PO_2 = H_3P + H_3PO_4$.

Phosphorous acid H_3PO_3, results from the slow oxidation of phosphoretted hydrogen or phosphorous aldehyd H_3P. Conversely,

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when phosphorous acid is acted upon by zinc, or zinc and sulphuric acid, it is deoxidated into phosphoretted hydrogen. Phosphorous acid, by exposure to air, acquires oxygen, and is converted into phosphoric acid. When heated by itself, it breaks up into phosphoric acid and phosphoretted hydrogen: $4H_3PO_3 = H_3P + 3H_3PO_4$.

Phosphoric acid H_3PO_4, results from the combustion of phosphoretted hydrogen in air or oxygen; and from the decomposition by heat, and direct oxidation of hypophosphorous and phosphorous acids. Phosphoric acid is much more stable than either of the other two acids, but like them may be made to yield phosphoretted hydrogen by deoxidation. This result can be effected by treatment with potassium or sodium.

Although the three acids of phosphorus are all terhydric, yet phosphoric acid alone is properly tribasic, or capable of having its three atoms of hydrogen displaced by metal. Phosphorous acid is bibasic, and hypophosphorous acid monobasic, or the former can lose two, and the latter but one of its hydrogen atoms, by an equivalent metallic substitution. Hence, while hypophosphorous acid forms but one class of salts, represented by the formula MH_2PO_2; phosphorous acid forms two classes, represented respectively by the formulæ M_2HPO_3 and MH_2PO_3; and phosphoric acid forms three classes, represented respectively by the formulæ M_3PO_4, M_2HPO_4, and MH_2PO_4. It is observable that although we have no representative of phosphorous acid in which the three hydrogen atoms are replaced by metal, yet that we have representatives in which these three atoms are replaced by a compound radicle; for example, phosphorous ether Et_3PO_3, corresponding to phosphoric ether Et_3PO_4.

We are acquainted with a few members of the class of sulphoxiphosphates M_3PO_3S, salts which have been already referred to. They may be viewed as phosphates M_3PO_4, in which one atom of oxygen is displaced by one of sulphur; so as to parallel the relations subsisting between the thiosulphates M_2SO_3S, and the oxisulphates M_2SO_4. We are also acquainted with hypophosphites, phosphites, and phosphates, in which all the oxygen atoms are displaced by sulphur.

There are two anhydrides of phosphorus, namely, phosphoric anhydride P_2O_5, and phosphorous anhydride P_2O_3. Hypophosphorous anhydride P_2O, is unknown; but all three sulphur-compounds have been described. Phosphorous anhydride is obtained by burning phosphorus in a limited supply of dry air, and phos-

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phoric anhydride by burning phosphorus in an excess of dry air, or of oxygen. Both compounds occur as white amorphous solids, which react violently with water to form their respective hydrates or acids:—

$$P_2O_3 + 3H_2O = 2H_3PO_3.$$
$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

The acids, however, have not been made to yield up water so as to reproduce the anhydrides.

The phosphorous and phosphoric chloraldehyds Cl_3P, and Cl_3PO respectively, react with water after the manner of chloraldehyds generally, to form their corresponding acids, as already described:—

$$3H_2O + Cl_3P = 3HCl + H_3PO_3.$$
$$3H_2O + Cl_3PO = 3HCl + HP_3O_4.$$

We have another chloro-representative of phosphoric aldehyd in the pentachloride of phosphorus Cl_5P, or Cl_3PCl_2, which also reacts with water to form phosphoric and chlorhydric acids, as we have seen:—

$$4H_2O + Cl_5P = 5HCl + H_3PO_4.$$

The compounds known as metaphosphoric and pyrophosphoric acids, and their corresponding salts, will be considered under the head of phosphoric acid and the phosphates.

(312) Suboxide of Phosphorus.—When phosphorus is burnt in air or oxygen, a solid orange-coloured matter is left behind, which slowly deliquesces, with formation of phosphorous acid. A similar substance is obtained, in larger quantity, by passing a current of oxygen gas through melted phosphorus covered by some depth of hot water. This body, when dried by pressure between filtering paper, and freed from phosphorus by treatment with bisulphide of carbon, leaves a dark red residue, which has been described as a definite oxide of phosphorus, but is now generally thought to be amorphous phosphorus contaminated with a little phosphoric acid. Leverrier noticed that when small pieces of phosphorus, covered by a layer of trichloride of phosphorus, were exposed to air, a peculiar yellow matter, soluble in water, was produced. At an increased temperature, the solution decomposed into phosphoric acid and a flocculent substance, which, when dried in vacuo over oil of vitriol, left a canary-yellow powder, the composition of which was represented by the formula P_4O. It could be preserved for any length of time in dry air. When heated, it

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acquired a bright red colour, but was unaffected in composition by a temperature of 300°. When more strongly heated it took fire.

Hypophosphorous Acid and Salts.

(313) Hypophosphorous Acid. *Sym.* H_3PO_2; *p. n.* 66.—Solution of hypophosphite of barium is decomposed by an equivalent quantity of sulphuric acid, according to the equation,

$$2BaH_2PO_2 + H_2SO_4 = 2H_3PO_2 + Ba_2SO_4.$$

The clear liquid is filtered off from the precipitated sulphate of barium and evaporated down. Or, solution of hypophosphite of lead is precipitated with sulphuretted hydrogen, and the filtrate evaporated down.

Hypophosphorous acid is a viscid uncrystallisable liquid, having a strongly acid reaction. When heated, it is decomposed into phosphoric acid and phosphoretted hydrogen:—

$$2H_3PO_2 = H_3PO_4 + H_3P.$$

Its solution in water constitutes a colourless mobile liquid, which, by exposure to air, becomes oxidised into phosphorous and phosphoric acids. Aqueous hypophosphorous acid reduces solutions of silver and gold, with precipitation of the respective metals. It also reduces solution of corrosive sublimate, with precipitation of either calomel or mercury according to the proportion of acid used. Hypophosphorous acid undergoes a remarkable reaction with salts of copper. This decomposition, first pointed out by Wurtz, distinguishes hypophosphorous from phosphorous acid, which it otherwise much resembles. When solutions of hypophosphorous acid and sulphate of copper are heated together to the temperature of 55°—60°, a solid insoluble subhydride of copper Cu_2H, is precipated. At a boiling temperature, this compound is decomposed into hydrogen gas and metallic copper. When hypophosphorous acid is mixed with zinc and sulphuric acid, phosphoretted hydrogen gas is liberated.

(314) Hypophosphites. *Sym.* MH_2PO_2.—*a.* These salts may be prepared by neutralising the acid with bases. In this way hypophosphite of lead is usually obtained. *β.* They may also be procured by boiling phosphorus in alkaline solutions. Thus, when phosphorus is boiled with lime-water or baryta-water, we have the reaction:—

$$3BaHO + P_4 + 3H_2O = 3BaH_2PO_2 + H_3P.$$

The hypophosphite may be crystallised out by cautious evapora-

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tion. When phosphorus is boiled with an aqueous solution of hydrate of potassium, a similar reaction takes place, but much phosphate of potassium is formed in addition. Such is not the case, however, when an alcoholic solution of hydrate of potassium is employed. When phosphorus is heated with anhydrous lime, strontia, or baryta, certain ill-defined compounds, known as the phosphides of calcium, strontium, and barium respectively, are obtained. By the reaction of water upon these compounds, phosphoretted hydrogen and a hypophosphite are produced. The ultimate result appears to be much the same whether the compound of lime and phosphorus, or a mixture of lime and phosphorus, is acted upon by water. γ. Many hypophosphites are produced by double decomposition. Thus, oxalate of magnesium boiled in solution of hypophosphite of calcium, yields oxalate of calcium, which is precipitated, and hypophosphite of magnesium, which is dissolved in the liquid:—

$$Mg_2C_2O_4 + 2CaH_2PO_2 = Ca_2C_2O_4 + 2MgH_2PO_2.$$

In a similar manner, hypophosphite of barium may be decomposed by soluble sulphates.

Hypophosphite of magnesium $MgH_2PO_2.3H_2O$, crystallizes in brilliant, efflorescent, regular octahedrons; and, like the hypophosphites of nickel, cobalt, and ferrosum, contains three atoms of crystallization-water. The hypophosphites of sodium, calcium, and barium are usually anhydrous; but the barium-salt is also known in the hydrated state.

The hypophosphites are crystallizable salts, soluble in water, and many of them in alcohol also. When dry, they are permanent in the air, but their solutions, when exposed, gradually become oxidised, particularly at the boiling temperature. When boiled in alkaline liquids, they are decomposed into phosphate and hydrogen:—

$$KH_2PO_2 + 2KHO = K_3PO_4 + H_4.$$

The dry salts, when heated, undergo decomposition and yield phosphoretted hydrogen, whence their ready inflammability. The hypophosphites, particularly at increased temperatures, act as powerful reducing agents.

Phosphorous Anhydride, Acid, and Salts.

(315) Phosphorous Anhydride. *Sym.* P_2O_3; *p. n.* 110.—This compound can only be obtained by the slow combustion of

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phosphorus. When phosphorus is exposed at ordinary temperatures to dry air or rarefied oxygen, it glows and becomes coated with phosphorous anhydride, but the reaction is very imperfect. The best mode of preparation consists in burning dry phosphorus in a very slow current of perfectly dry air. The anhydride then condenses beyond the phosphorus as a bulky amorphous sublimate. The ordinary combustion of phosphorus in air produces both phosphorous and phosphoric anhydrides, together with some oxide of phosphorus. (?) Phosphorous anhydride occurs in large white flakes: it is readily volatile, and evolves a garlic-like odour. When perfectly dry, it does not affect litmus paper. It absorbs atmospheric moisture with avidity, and thereby gives rise to a great development of heat. It behaves still more violently when sprinkled with water, in which it rapidly dissolves with a hissing noise, producing phosphorous acid: $P_2O_3 + 3H_2O = 2H_3PO_3$.

(316) Phosphorous Acid. *Sym.* H_3PO_3; *p.n.* 82. — *a.* This acid results from the reaction of the anhydride upon water, as we have just seen. *β.* Phosphorous acid is obtainable by the slow oxidation of its aldehyd H_3P. Thus, when phosphoretted hydrogen is allowed to stand over well aerated water, it is gradually absorbed, with production of phosphorous acid. Again, two volumes of phosphoretted hydrogen will quietly unite with three volumes of oxygen, when the explosion of the two gases is prevented by cooling. *γ.* Phosphorous acid is frequently made by merely exposing sticks of phosphorus to a moist atmosphere. Each stick is placed in a sort of test-tube, having a contracted opening at the bottom. Several of these tubes and sticks are arranged in a funnel, supported over a beaker or other vessel. By the action of a moist atmosphere, a dense acid liquid is gradually formed, which drains through the funnel into the beaker, while the sticks of phosphorus slowly disappear. The liquid produced contains both phosphorous and phosphoric acids. *δ.* Phosphorous acid results from the decomposition, by water, of phosphorous chloraldehyd or terchloride of phosphorus: $3H_2O + PCl_3 = H_3PO_3 + 3HCl$. A current of washed chlorine is slowly transmitted through three or four inches depth of melted phosphorus, covered by six or eight inches of water, so that each bubble of gas may be perfectly absorbed by the phosphorus. The terchloride, thereby produced, is at once decomposed by contact with the supernatant water. The chlorhydric acid set free in the reaction is expelled by evaporation. In the above experiment, it is important to avoid the slightest excess of chlorine, in order to prevent the formation of phosphoric acid.

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Phosphorous acid usually exists in the state of a thick uncrystallizable syrup; but it may be obtained in the form of crystals, by cooling a somewhat concentrated aqueous solution: both the syrup and the crystals are very deliquescent. When heated, they undergo decomposition into phosphoric acid and phosphoretted hydrogen: $4H_3PO_3 = 3H_3PO_4 + H_3P$. Hence the acid, when heated in air, undergoes vivid combustion. The aqueous solution of phosphorous acid is a strongly acid liquid, which, when exposed to the air, absorbs oxygen and is converted into phosphoric acid. It is a powerful reducing agent, and decomposes the salts of gold, silver, and mercury as readily as does hypophosphorous acid. When acted upon by zinc and sulphuric acid it evolves phosphoretted hydrogen.

(317) PHOSPHITES. *Sym.* MH_2PO_3 and M_2HPO_3.—These salts are obtained sometimes by acting on the acid with bases, sometimes by double decomposition with one another. The dimetallic sodium salt $Na_2HPO_3 . 5H_2O$, crystallizes in rhombohedral crystals containing five atoms of water. All phosphites are destroyed by heat, with production of free hydrogen, accompanied, in the case of bibasic salts, with some phosphoretted hydrogen. The phosphites are more stable salts than are the hypophosphites. Their solutions are tolerably permanent when exposed to air at ordinary temperatures, and are not decomposed by boiling with caustic alkali. They precipitate metallic gold, silver, mercury, and, at a boiling temperature, copper from their respective solutions. They also reduce sulphurous acid to the state of sulphydric acid, thus: —

$$3Na_2HPO_3 + H_2SO_3 = 3Na_2HPO_4 + H_2S.$$

The bibasic phosphites, with the exception of those of the alkali-metals, are sparingly soluble, and that of lead almost insoluble, in water; the acid phosphites, however, are more soluble. Solutions of the phosphites, unless very concentrated, do not precipitate the solution of a magnesian salt in aqueous ammonia and sal-ammoniac.

PHOSPHORIC ANHYDRIDE, ACID, AND SALTS.

(318) Phosphoric acid, H_3PO_4, is a very definite body, occurring in the form of hard, colourless, transparent crystals. It is a tribasic acid, and produces three distinct classes of salts, as shown below in the case of its sodium compounds:—

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H_3PO_4	Phosphoric, or orthophosphoric acid.
NaH_2PO_4	Monophosphate, or acid phosphate of sodium.
Na_2HPO_4	Diphosphate, or neutral phosphate of sodium.
Na_3PO_4	Triphosphate, or basic phosphate of sodium.

It also forms three corresponding ethers, thus :—

H_3PO_4	Phosphoric acid.
EtH_2PO_4	Ethyl-phosphoric acid.
Et_2HPO_4	Di-ethyl-phosphoric acid.
Et_3PO_4	Phosphoric ether.

Ethyl-phosphoric and di-ethyl-phosphoric acids have respectively the characters of bibasic and monobasic acids, but phosphoric ether is perfectly neutral. The monophosphates have a marked acid reaction, soluble triphosphates a marked alkaline reaction, while diphosphates are intermediate, but not indeed strictly neutral, being for the most part somewhat alkaline. It frequently happens that the three atoms of hydrogen in phosphoric acid are displaced by different metals or pseudo-metals. Thus the well-known reagent, microcosmic salt, or diphosphate of sodium and ammonium, is represented by the formula $Na(NH_4)HPO_4$.

(319) Metaphosphoric acid.—When ordinary monophosphate of sodium is heated to redness, it undergoes decomposition: water is expelled, and a new salt produced :—

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

This new salt is soluble in water, and its solution precipitates salts of the heavy and alkaline earth-metals. Thus, with nitrate of lead, we have the reaction :—

$$NaPO_3 + PbNO_3 = PbPO_3 + NaNO_3.$$

When this lead precipitate is suspended in water and decomposed by sulphuretted hydrogen, a new phosphoric acid is produced according to the following equation :—

$$2PbPO_3 + H_2S = 2HPO_3 + Pb_2S.$$

This new acid, or metaphosphoric acid, as it is termed, HPO_3, has properties quite distinct from those of ordinary phosphoric acid H_3PO_4, which, being the normal compound, is distinguished by the name of orthophosphoric acid. Both compounds are soluble in water, and possess well-marked acid characters. But metaphosphoric acid coagulates albumin, orthophosphoric acid does not. Metaphosphoric acid gives a white precipitate with neutral solu-

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tions of barium-salts; orthophosphoric acid does not give any, save on the addition of an alkali. Metaphosphoric acid gives a white precipitate with nitrate of silver solution; orthophosphoric acid does not give any, save on the addition of an alkali, and the precipitate then produced is yellow. In comparing the formulæ of metaphosphoric acid and the metaphosphates with those of orthophosphoric acid and the orthophosphates, it is observable that the former compounds differ from the latter by the want of an atom of water or an atom of base, thus :—

$$\begin{aligned} HPO_3 &= H_3PO_4 - H_2O. \\ BaPO_3 &= BaH_2PO_4 - H_2O. \\ NaPO_3 &= Na_2HPO_4 - NaHO. \\ PbPO_3 &= Pb_3PO_4 - Pb_2O. \\ AgPO_3 &= Ag_3PO_4 - Ag_2O. \end{aligned}$$

And we find experimentally that when metaphosphates gain an atom of water or base, they become orthophosphates; and, conversely, when the orthophosphates lose an atom of water or base, they become metaphosphates, as exemplified in the following instances:—

a. Solution of metaphosphoric acid becomes converted, slowly at ordinary temperatures, rapidly at a boiling heat, into orthophosphoric acid: $HPO_3 + H_2O = H^3PO_4$. *β.* Metaphosphate of barium, which is insoluble as such, dissolves in water, slowly at ordinary temperatures, rapidly at a boiling heat, with formation of monobasic orthophosphate of barium: $BaPO_3 + H_2O = BaH_2PO_4$. In a similar manner, a solution of metaphosphate of sodium becomes converted into monobasic orthophosphate of sodium; or, if the solution be rendered alkaline, into dibasic or tribasic orthophosphate. *γ.* The metaphosphate of a heavy metal, silver or lead for example, when boiled with water, becomes converted into tribasic orthophosphate of metal and orthophosphoric acid: $3AgPO_3 + 3H_2O = Ag_3PO_4 + 2H_3PO_4$. If the water be rendered alkaline, orthophosphates of alkali-metal are formed instead of orthophosphoric acid. *δ.* When any metaphosphate is fused with an oxide, hydrate, or carbonate, it becomes a tribasic orthophosphate: $NaPO_3 + Na_2CO_3 = Na_3PO_4 + CO_2$.

On the other hand (*ε*), when orthophosphoric acid is heated to dull redness, it loses water, and is transformed into metaphosphoric acid: $H_3PO_4 - H_2O = HPO_3$. *ζ.* Again, when a monobasic orthophosphate is heated to redness, it loses water, and is converted into a metaphosphate: $NaH_2PO_4 - H_2O = NaPO_3$.

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Or if one of the bases of a dibasic orthophosphate be volatile, we likewise have a metaphosphate produced by heating the salt to redness, thus:—

$$Na(NH_4)HPO_4 - NH_4HO = NaPO_3.$$

η. When a tribasic orthophosphate is fused with a fixed anhydride, silicic or boric, for example, we have a metaphosphate produced, thus:—

$$SiO_2 + Na_3PO_4 = Na_2SiO_3 + NaPO_3.$$

Phosphoric anhydride, when allowed to absorb water spontaneously, or when acted upon by cold water, produces metaphosphoric acid: $P_2O_5 + H_2O = 2HPO_3$. But orthophosphoric acid is always formed to a considerable extent, especially when the anhydride is acted upon by hot water: $P_2O_5 + 3H_2O = 2H_3PO_4$. It seems probable, however, that even in this instance metaphosphoric acid is first produced, which, by the subsequent absorption of water into its molecule, becomes orthophosphoric acid. When phosphoric anhydride is fused with the salt of a volatile anhydride, we have an ortho- or meta-phosphate produced, according to the facility with which the volatile anhydride can be expelled from the base. Thus with phosphoric anhydride and sulphate of magnesium we have the reaction:—

$$P_2O_5 + 3Mg_2SO_4 = 2Mg_3PO_4 + 3SO_3.$$

But by substituting sulphate of potassium for sulphate of magnesium, we have the reaction:—

$$P_2O_5 + K_2SO_4 = 2KPO_3 + SO_3.$$

In comparing metaphosphates and orthophosphates with one another, it is observable that metaphosphates stand to orthophosphates in the relation of anhydro-salts; while orthophosphates stand to metaphosphates in the relation of superbasic salts. Thus, when tribasic orthophosphate of sodium is heated with phosphoric anhydride, we have a metaphosphate produced:—

$$Na_3PO_4 + P_2O_5 = 3NaPO_3.$$

Again, when metaphosphate of sodium is heated with charcoal, it breaks up into tribasic orthophosphate, which is irreducible by the charcoal, and phosphoric anhydride, which is decomposed by the charcoal into carbonic oxide and phosphorus vapour:—

$$3NaPO_3 + C_5 = Na_3PO_4 + 5CO + P_2.$$

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Conversely, when a metaphosphate is heated with a base, it becomes an orthophosphate, as we have already seen. Moreover, the tribasic orthophosphates possess several of the characters of superbasic salts. Thus they have a strongly alkaline reaction, and yield up one of their three atoms of base to such a feeble acid as the carbonic, and even to an excess of water. Again, the addition of a soluble superbasic salt to the solution of a metaphosphate produces an orthophosphate. Thus, when trisacetate of lead is added to metaphosphate of sodium, a considerable proportion of orthophosphate of lead is always formed, thus:—

$$NaPO_3 + C_2H_3PbO_2.Pb_2O = Pb_3PO_4 + C_2H_3NaO_2.$$

The existence of two distinct classes of salts, differing from one another by an atom of base or basic water, is not peculiar to the phosphates, but seems to prevail, to a greater or less extent, among many polybasic salts. Thus we have two distinct classes of silicates comparable to the two classes of phosphates, as shown below:—

KPO_3 Metaphosphate.	K_3PO_4 Orthophosphate.
K_2SiO_3 Metasilicate.	Mg_4SiO_4 Orthosilicate.

These relations seem to be paralleled to some extent in the nitrates and carbonates; only that while orthophosphates M_3PO_4, and orthosilicates M_4SiO_4, constitute the ordinary forms of phosphates and silicates respectively, metanitrates MNO_3, and metacarbonates M_2CO_3, constitute the ordinary forms of nitrates and carbonates respectively.

$PbNO_3$ Metanitrate.	Pb_2HNO_4 Orthonitrate.
Fe_2CO_3 Metacarbonate.	Cu_3HCO_4 Orthocarbonate.

It is worthy of note that metasalts, although formulated with three atoms of oxygen, differ strikingly from normal teroxysalts in the circumstance of their inoxidability. Thus chlorates, iodates, sulphites, selenites, phosphites, arsenites, lactates, &c., are all capable of direct or indirect oxidation, as indicated below; but nitrates, carbonates, metaphosphates, and metasilicates are absolutely inoxidisable:—

$MClO_3$	MIO_3	M_2SO_3	M_2SeO_3	M_3PO_3	M_3AsO_3	$C_3H_4M_2O_3$, &c.
$MClO_4$	MIO_4	M_2SO_4	M_2SeO_4	M_3PO_4	M_3AsO_4	$C_3H_4M_2O_4$, &c.

(320) Pyrophosphoric acid. — Intermediate between orthophosphates and metaphosphates we have at least three distinct

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classes of salts, of which the most important are the pyrophosphates or paraphosphates $M_4P_2O_7$. These salts may be viewed as compounds formed by the union of an atom of orthophosphate with an atom of metaphosphate: $M_4P_2O_7 = M_3PO_4 + MPO_3$. The four atoms of base in the pyrophosphates may be constituted of the same or of different metals. In pyrophosphates with two different basic metals, it is most usual to find three equivalents of base constituted of the one metal, and one equivalent of base constituted of the other, as is the case, for example, in the double pyrophosphate of sodium and copper $Cu_3NaP_2O_7$. The tendency to form salts of this description seems to favour the notion that pyrophosphates are compounds of orthophosphate and metaphosphate. Thus the above double pyrophosphate might be represented by the formula $Cu_3PO_4.NaPO_3$

Pyrophosphate of sodium is produced by heating dibasic orthophosphate of sodium to redness, thus:—

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

The new salt dissolves in water, and its solution precipitates insoluble pyrophosphates from soluble lead and silver salts, thus:—

$$Na_4P_2O_7 + 4PbNO_3 = Pb_4P_2O_7 + 4NaNO_3.$$

This pyrophosphate of lead, when acted upon by sulphuretted hydrogen, yields pyrophosphoric acid:—

$$Pb_4P_2O_7 + 2H_2S = H_4P_2O_7 + 2Pb_2S.$$

Pyrophosphoric acid presents properties distinct alike from those of metaphosphoric and of orthophosphoric acid. Thus, unlike metaphosphoric acid, it does not precipitate albumin, nor yet neutral solutions of barium and silver salts. In these properties it agrees with orthophosphoric acid; but its neutralised solution gives with nitrate of silver a white precipitate, $Ag_4P_2O_7$, whereas that of orthophosphoric acid produces a yellow precipitate, Ag_3PO_4, as we have previously observed.

a. The production of a pyrophosphate from an orthophosphate by the loss of water, has just been referred to. *β.* Conversely, when a pyrophosphate is heated with water or a base, we have orthophosphates reproduced:—

$$Na_4P_2O_7 + H_2O = 2NaHPO_4.$$
$$Na_4P_2O_7 + 2NaHO = 2Na_3PO_4 + H_2O.$$

These correlations of orthophosphates and pyrophosphates are

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paralleled in their corresponding acids. γ. Thus when orthophosphoric acid is heated to a temperature of 215°, it is converted almost entirely into pyrophosphoric acid:—

$$2H_3PO_4 - H_2O = H_4P_2O_7 + H_2O.$$

δ. Conversely, when pyrophosphoric acid is boiled with water, it becomes orthophosphoric acid:—

$$H_4P_2O_7 + H_2O = 2H_3PO_4.$$

ε. When pyrophosphoric acid is heated to dull redness, it becomes metaphosphoric acid:—

$$H_4P_2O_7 = 2HPO_3 + H_2O.$$

The converse reaction, however, has not been effected, metaphosphoric acid by the absorption of water passing directly into the state of orthophosphoric acid. ζ. But when a metaphosphate is treated with the proper proportion of a hydrate, oxide, or carbonate, it becomes a pyrophosphate:—

$$2NaPO_3 + Na_2CO_3 = Na_4P_2O_7 + CO_2.$$

(321) Fleitmann and Henneberg obtained a salt having the composition $Na_3PO_4.3NaPO_3$, or $Na_6P_4O_{13}$, by fusing together an atom of pyrophosphate of sodium $Na_3PO_4.NaPO_3$, with two atoms of metaphosphate $NaPO_3$. This compound is soluble without decomposition in a small quantity of hot water, and crystallizes from its solution by evaporation over oil of vitriol. An excess of hot water decomposes it, but its cold aqueous solution is moderately permanent. Insoluble phosphates of similar constitution may be obtained from the sodium-salt by double decomposition. Fleitmann and Henneberg produced another crystallizable, but very unstable, salt, having the composition $Na_3PO_4.9NaPO_3$, or $Na_{12}P_{10}O_{31}$, by fusing together one atom of pyrophosphate of sodium with eight atoms of the metaphosphate; and insoluble phosphates of similar constitution were obtained from it by double decomposition. The relative proportions of base and anhydride in these different salts is best shown by according to them all the quantity of base contained in the most complex member of the series, that is to say, six atoms, as in the following table:—

Orthophosphate	$6M_2O.2P_2O_5 = 4M_3PO_4.$
Pyrophosphate	$6M_2O.3P_2O_5 = 3M_4P_2O_7.$
Fleitmann and Henneberg (*a*)	$6M_2O.4P_2O_5 = 2M_6P_4O_{13}.$
Fleitmann and Henneberg (*b*)	$6M_2O.5P_2O_5 = 1M_{12}P_{10}O_{31}.$
Metaphosphate	$6M_2O.6P_2O_5 = 12MPO_3.$

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(322) PHOSPHORIC ANHYDRIDE. *Sym.* P_2O_5; *p. n.* 142. This compound is obtained by burning dry phosphorus in an excess of dry air or oxygen. The combustion is usually effected in a large glass globe having three wide necks, one leading perpendicularly upwards, the other two opening laterally opposite each other. A wide glass tube, open at both ends, and dipping more than half way into the globe, is fixed in the perpendicular neck. The top of this tube is provided with a cork, while, from its bottom, a porcelain capsule, containing a piece of phosphorus, is suspended by means of platinum wire. One of the lateral openings of the globe communicates with a U-tube, containing pumice and oil of vitriol, to dry the air, while the other lateral opening communicates with one neck of a large Woulfe's bottle, destined to receive the product. The phosphorus in the capsule is then ignited by a hot wire, the cork inserted in the perpendicular tube, and a current of dry air passed through the apparatus by an aspirator attached to the second neck of the Woulfe's bottle, or by a blower connected with the U-tube, or by other means. From time to time fresh pieces of phosphorus are dropped into the capsule through the perpendicular tube, which is re-corked after each addition. The phosphoric anhydride produced by the combustion condenses as a white deposit in the globe and Woulfe's bottle. In consequence of the difficulty of removing the deposit from a Woulfe's bottle, it is found convenient to substitute for it an ordinary wide-mouthed bottle furnished with a cork having two apertures.

Phosphoric anhydride occurs as a snow-white, flocculent, amorphous deposit, which fuses at a red heat, and sublimes below a white heat. When free from phosphorous anhydride, it is inodorous; and when perfectly dry does not affect litmus paper. It is extremely deliquescent, and unites with the water it absorbs to form metaphosphoric acid. It dissolves in water with a hissing noise and great development of heat, but some few flakes of the anhydride often remain undissolved for upwards of an hour. Phosphoric anhydride is decomposed, when heated with charcoal, into carbonic oxide and phosphorus. It is also decomposed when heated with readily oxidisable metals. At a red heat, it expels the more volatile anhydrides from their salts, so as to produce an orthophosphate, pyrophosphate, or metaphosphate, according to the facility with which the volatile anhydride can be expelled.

(323) METAPHOSPHORIC ACID. *Sym.* HPO_3; *p. n.* 80. — *a.* This acid may be obtained by acting upon the anhydride with cold water, as we have just seen. *β.* It may also be procured by

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heating pyrophosphoric or orthophosphoric acid to redness. Orthophosphate of ammonium may be substituted for the orthophosphoric acid, but the last portions of ammonia are expelled with great difficulty. γ. Or it may be made by acting upon certain of its salts with some other acid. Thus, when metaphosphate of lead, suspended in water, is heated with a current of sulphydric acid gas, we have sulphide of lead and metaphosphoric acid produced, $2PbPO_3 + H_2S = 2HPO_3 + 2Pb_2S$. Metaphosphoric acid is a transparent, colourless, glassy, uncrystallisable, deliquescent solid, which dissolves slowly, although to a considerable extent, in water, forming a strongly acid liquid. Its solution gives white precipitates with solutions of albumin, nitrate of silver, and chloride of barium. Aqueous metaphosphoric acid is converted by absorption of water, slowly at ordinary temperatures, rapidly at a boiling heat, into orthophosphoric acid, without passing through the intermediate stage of pyrophosphoric acid. Metaphosphoric acid volatilizes completely at a bright red heat, but, according to Rose, its composition varies during the volatilization, the last portions volatilized consisting of metaphosphoric acid and phosphoric anhydride.

(324) METAPHOSPHATES. *Sym.* MPO_3. — *a.* These salts may be produced by treating the acid with bases (*vide infra*). β. Metaphosphates are generally made by igniting a monobasic orthophosphate of a fixed base, or a dibasic orthophosphate having one fixed and one volatile base, or an acid pyrophosphate. Metaphosphate of sodium is most readily prepared by heating pure microcosmic salt or dibasic orthophosphate of sodium and ammonium to redness, thus:—

$$Na(NH_4)HPO_4 = NaPO_3 + (NH_4)HO.$$

γ. Many metaphosphates are made by double decomposition. In this way, the insoluble metaphosphates of silver, lead, and barium are produced from metaphosphate of sodium. Again, metaphosphate of ammonium may be made by treating metaphosphate of lead with sulphide of ammonium. δ. Metaphosphates also result from heating tribasic orthophosphates or dibasic pyrophosphates with the proper proportions of phosphoric anhydride or phosphoric acid.

The metaphosphates of alkali-metal are fusible soluble salts, not usually crystalline. The precipitated metaphosphates have a more or less gelatinous aspect: precipitated metaphosphate of lead is fusible in boiling water. The metaphosphates are readily decom-

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posed by other acids: thus even acetic acid will decompose metaphosphate of sodium, as shown by the fact that a mixture of acetic acid and metaphosphate of sodium will precipitate albumin, although neither reagent will separately produce that effect. The decomposition of metaphosphate of lead by sulphydric acid has been already described as a process for the formation of metaphosphoric acid. The circumstances under which metaphosphates become pyrophosphates and orthophosphates have been previously referred to.

(325) The metaphosphates are remarkable for the exhibition of very different properties, according to the modes in which they are prepared. These differences are considered to depend upon the existence of several polymeric modifications. *α.* Metaphosphate of sodium is usually obtained in the form of a vitreous mass. It is soluble in water, and precipitates gelatinous metaphosphates from the salts of the heavy and alkaline-earth metals. *β.* When a considerable quantity of fused metaphosphate of sodium is allowed to cool very slowly, the salt, in solidifying, acquires a beautifully crystalline structure. When this mass is acted upon by a slight excess of warm water, the liquid separates into two layers. The larger stratum contains the crystalline, and the smaller stratum the ordinary vitreous salt. The solution of the former variety gives hydrated crystalline precipitates with salts of the heavy metals. The formulæ of the crystalline metaphosphates of silver and lead, thus produced, are respectively $3AgPO_3.H_2O$ and $2PbPO_3.H_2O$.

γ. When oxide of copper and a slight excess of solution of phosphoric acid are heated together to the temperature of 350°, an insoluble crystalline powder is produced. When this powder is acted upon by alkaline sulphides, corresponding metaphosphates of alkali-metal are obtained. These are soluble crystallizable salts which, when heated to the temperature of 250°, undergo a certain change, whereby they are rendered quite insoluble. The *γ*-metaphosphates have a marked tendency to form crystalline double salts. Thus concentrated solutions of *γ*-metaphosphate of sodium and chloride of potassum, or of *γ*-metaphosphate of potassium and chloride of sodium, furnish by double decomposition a crystalline precipitate having the formulæ $\left.\begin{matrix}NaPO_3\\KPO_3\end{matrix}\right\}H_2O$. Again, concentrated solutions of *γ*-metaphosphate of ammonium and chloride of copper, when mixed together, deposit, on the addition of alcohol, blue crystalline needles, having the composition $\left.\begin{matrix}NH_4PO_3\\CuPO_3\end{matrix}\right\}2H_2O$.

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δ. When phosphoric acid and oxide of lead are heated together, a compound is obtained which, by decomposition with sulphide of sodium, furnishes a peculiar metaphosphate of sodium, characterised by the property of forming with water a viscid elastic mass, and with excess of water a gummy solution. Like the preceding variety, it produces double salts of two bases, in equal atomic proportions.

ε. Metaphosphates of this variety are remarkable for their insolubility in water. They may be obtained by heating the γ-metaphosphates to 250°, as already observed; or by adding excess of phosphoric acid to solutions of sulphates or nitrates, evaporating the liquids to dryness, and heating the residues to 316° and upwards. They occur as crystalline anhydrous powders.

(326) PYROPHOSPHORIC ACID. *Sym.* $H_4P_2O_7$; *p.n.* 178.—This acid usually occurs as a soft glass, but has been obtained in opaque semi-crystalline masses. *α.* It may be procured by evaporating a solution of orthophosphoric acid until its temperature rises to 213°; but the product of the operation is always contaminated with unchanged orthophosphoric acid. *β.* Pyrophosphoric acid is generally prepared by decomposing certain of its salts with some other acid. Thus when pyrophosphate of lead, suspended in water, is treated with sulphydric acid gas, we obtain, by double decomposition, sulphide of lead and aqueous pyrophosphoric acid:—

$$Pb_4P_2O_7 + 2H_2S = H_4P_2O_7 + Pb_2S.$$

Pyrophosphoric acid becomes metaphosphoric acid when heated to redness, and orthophosphoric acid when boiled with water. This last conversion takes place very slowly at ordinary temperatures; so that, according to Graham, the aqueous acid may be kept unaltered for even half a year. Solution of pyrophosphoric acid is a strongly acid liquid which does not precipitate solutions of albumin, chloride of barium, or nitrate of silver, but which, after neutralization, gives white precipitates with the last two reagents.

(327) PYROPHOSPHATES. *Sym.* $M_4P_2O_7$.—*α.* Tetrabasic pyrophosphates may be obtained, as we have already seen, by igniting dibasic orthophosphates; or by heating any form of phosphoric acid with a quantity of oxide, hydrate, or carbonate, sufficient to furnish two atoms of basic metal; or by heating a metaphosphate with a quantity of oxide, hydrate, or carbonate, sufficient to furnish one atom of basic metal. *β.* Pyrophosphates may be procured by neutralising pyrophosphoric acid with bases. The acid salts may

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be made by neutralising one quantity of pyrophosphoric acid with base, and then adding thereto one-third, or one, or three more proportions of the acid. In this way, salts having the respective formulæ $M_3HP_2O_7$, $M_2H_2P_2O_7$, $MH_3P_2O_7$, may be obtained. γ. Many pyrophosphates are formed by double decomposition. Solutions of pyrophosphates, even when very much diluted, give precipitates with salts of calcium, barium, lead, and silver. Precipitated pyrophosphate of silver occurs as a chalky-white powder, very different in its appearance from the somewhat gelatinous white precipitate of metaphosphate of silver. Pyrophosphate of lead, precipitated from solution of nitrate or acetate of lead, serves for the production of pyrophosphoric acid, by treatment with sulphydric acid, as we have already seen. The precipitates produced by pyrophosphate of sodium in solutions of copper, nickel, &c. are double salts, containing one proportion of sodium to three proportions of the other metal, thus :—

$$Na_4P_2O_7 + 3CuCl = Cu_3NaP_2O_7 + 3NaCl.$$

Among tetrabasic pyrophosphates, those of the alkali-metals only are soluble in water. Their solutions have a slightly alkaline reaction, and cannot be heated without undergoing conversion into orthophosphates. The circumstances under which pyrophosphates become orthophosphates and metaphosphates have been previously considered.

(328) ORTHOPHOSPHORIC ACID. *Sym.* H_3PO_4; *p. n.* 98.—*a.* This acid may be made by acting with boiling water upon phosphoric anhydride, metaphosphoric acid, and pyrophosphoric acid, as we have already seen. β. Orthophosphoric acid results from the combustion of phosphoretted hydrogen in air or oxygen; and likewise from the oxidation, spontaneous or otherwise, of hypophosphorous and phosphorous acids. γ. It is also produced by the action of water on phosphoric chloraldehyd :—

$$PCl_3O + 3H_2O = H_3PO_4 + 3HCl.$$

When pentachloride of phosphorus is acted upon by a small quantity of water, we at first have phosphoric chloraldehyd formed, which a further addition of water decomposes as above :—

$$PCl_5 + H_2O = PCl_3O + 2HCl.$$
$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl.$$

An excess of chlorine gas may be passed through phosphorus,

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melted under water, whereby the production and decomposition of the pentachloride take place almost simultaneously. The phosphoric acid may be freed from chlorhydric acid by ebullition.

δ. Orthophosphoric acid is frequently prepared by the oxidation of phosphorus with nitric acid. One part of phosphorus is heated in a retort with about fifteen parts of dilute nitric acid, sp. gr. 1·2, until it is dissolved. The distillate, which contains some phosphorous acid, is then returned to the retort, and the entire liquid evaporated down. At a certain degree of concentration a very considerable effervescence occurs, due to the oxidation of the phosphorous acid into phosphoric acid. Small quantities of nitric acid are then added from time to time, until the last addition no longer produces any effervesence, after which the liquid is evaporated to expel the nitric acid. If, as frequently happens, this evaporation is carried so far as to produce pyrophosphoric or even metaphosphoric acid, the residue is to be boiled for a short time in water, whereby these last two acids are reconverted into orthophosphoric acid. ε. Orthophosphoric acid may be prepared by acting upon certain of its salts with some other acid. Thus, when orthophosphate of lead, suspended in water, is acted upon by a current of sulphydric acid gas, we have sulphide of lead and orthophosphoric acid produced :—

$$2Pb_3PO_4 + 3H_2S = 2H_3PO_4 + 3Pb_2S.$$

Berzelius prepares his phosphate of lead by adding acetate of lead to a solution of bone earth, or crude orthophosphate of calcium, in a minimum quantity of hot dilute nitric acid. The precipitate is then washed with hot water, ignited, and decomposed with sulphuric acid : $2Pb_3PO_4 + 3H_2SO_4 = 2H_3PO_4 + 3Pb_2SO_4$. The solution of orthophosphoric acid so produced is evaporated to dryness, and the residue ignited to expel sulphuric acid, then dissolved in boiling water and treated with sulphydric acid gas to remove every trace of lead.

Liebig and Gregory obtain orthophosphoric acid by acting upon bone earth with excess of sulphuric acid, and extracting the resulting mass with water. By filtration, an impure solution of orthophosphoric acid is separated from the comparatively insoluble residue of gypsum :—

$$2Ca_3PO_4 + 3H_2SO_4 + 6H_2O = 2H_3PO_4 + 3(Ca_2SO_4.2H_2O).$$

The acid solution is concentrated to a small bulk and more sulphuric acid added, whereby a further precipitate of gypsum

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is formed, which, after dilution of the liquid with water, is separated on a filter. This operation of evaporation to a small bulk, treatment with sulphuric acid, dilution with water, and filtration, is repeated a second and even a third time, until the lime is completely got rid of. The acid is next evaporated to a syrup, and gently ignited to expel the sulphuric acid. It is then dissolved in a small quantity of boiling water, and the liquid, after evaporation, maintained for about half an hour at a temperature of 315°, whereby a white powder is deposited. The mass when cold is extracted with cold water, and the liquid filtered. The deposit consists of a double metaphosphate of magnesium and sodium $3MgPO_3.NaPO_3$. The filtrate, when boiled, constitutes a solution of orthophosphoric acid, contaminated indeed with a trace of sodium, but otherwise pure.

(329) Orthophosphoric acid may be procured, in the form of hard transparent prismatic crystals, by concentrating its solution to a thin syrup, and then allowing it to stand for some time over oil of vitriol. Solution of orthophosphoric acid may be heated to 160° without altering the character of the acid. At 213° it is converted principally into pyrophosphoric acid. At temperatures above this metaphosphoric acid makes its appearance, and, after the application of a full red heat, constitutes the entire residue. Aqueous orthophosphoric acid has a strongly acid reaction, and at a boiling temperature decomposes the salts of most volatile acids. It does not precipitate solutions of albumin, chloride of barium, nitrate of silver, or sesquichloride of iron. After complete or partial neutralization, however, it gives a white precipitate with chloride of barium, a yellow precipitate with nitrate of silver, and a buff-coloured precipitate with sesquichloride of iron. This form of phosphoric acid and its soluble salts gives, with solution of sulphate of magnesium in ammonia and sal-ammoniac, a characteristic crystalline precipitate, consisting of $Mg_2(NH_4)PO_4.6H_2O$, by the formation of which the presence of orthophosphoric acid in any substance is most usually detected. Arsenic acid and the arsenates produce a similar precipitate, $Mg_2(NH_4)AsO_4.6H_2O$. The solutions of these two acids and their salts have the exclusive property of producing a precipitate in ammoniacal solutions of magnesium-salts. The phosphoric precipitate, when ignited, is converted into pyrophosphate of magnesium:—

$$2Mg_2NH_4PO_4 = Mg_4P_2O_7 + 2NH_3 + H_2O.$$

From the weight of this residue the quantity of orthophosphoric acid present in any substance is usually estimated.

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(330) ORTHOPHOSPHATES. *Sym.* MH_2PO_4, *monometallic, or biacid salt;* M_2HPO_4, *bimetallic, or monacid salt;* M_3PO_4, *trimetallic, or normal salt.* The orthophosphates constitute a very extensive and important class of salts, the principal members of which, together with some super-basic compounds, are formulated in the following table: —

KH_2PO_4	
K_3PO_4	
$NaH_2PO_4 . H_2O$	
$Na_2HPO_4 . 7H_2O$	
$Na_2HPO_4 . 12H_2O$	
$Na_3PO_4 . 12H_2O$	
$KNaHPO_4 . H_2O$	
$NH_4H_2PO_4$	
$(NH_4)_2HPO_4$	
$NaNH_4HPO_4 . 4H_2O$	Microcosmic salt.
BaH_2PO_4	
Ba_3PO_4	
CaH_2PO_4	
$Ca_2HPO_4 . 2H_2O$	Bödecker's salt.
Ca_3PO_4	Apatite?
$Mg_2HPO_4 . 7H_2O$	
$Mg_2NH_4PO_4 . H_2O$	
$Mg_2NH_4PO_4 . 6H_2O$	Triple phosphate.
$Zn_2HPO_4 . H_2O$	
$Zn_3PO_4 . H_2O$	
$Zn_2NH_4PO_4 . H_2O$	
$MnH_2PO_4 . H_2O$	
$Mn_2HPO_4 . 3H_2O$	
$Mn_2NH_4PO_4 . H_2O$	
Fe_2HPO_4	
$Fe_3PO_4 . H_2O$	Vivianite.
$Fe_2NH_4PO_4 . H_2O$	
$(FeMnLi)_3PO_4$	Triphylline.
$(MnFe)_3PO_4 . MnFeO$	Triplite.
$(MnFeFfe)_3PO_4 . xH_2O$	Hureaulite.
$Ffe'''PO_4 . 2H_2O$	
$Ffe'''PO_4 . Ffe'''H_3O_3$	Green ironstone.
$Ffe'''PO_4 . Ffe'''H_3O_3 . 9H_2O$	Delvauxite.
$Cu_3PO_4 . CuHO$	Apherese.
$Cu_3PO_4 . 3CuHO$	Phosphochalcite.
$2(Cu_2HPO_4) . 3H_2O$	Trombolite.
$2(Cu_2HPO_4) . 2CuHO . H_2O$	Liebethenite.
Hhg_2HPO_4	
Hg_2HPO_4	
Pb_2HPO_4	Bödecker's salt.
Pb_3PO_4	Pyromorphite?
Ag_3PO_4	
$Bi'''PO_4$	
$All'''PO_4$	
$All'''PO_4 . All'''H_3O_3 . H_2O$	Turquoise.
$All'''PO_4 . All'''H_3O_3 . 6H_2O$	Wavellite?
$(UO)H_2PO_4$	
$(UO)_2HPO_4$	
$(UO)_2NH_4PO_4$	

Among trimetallic phosphates, those of the alkali-metals are alone soluble in water. Their solutions have a strongly alkaline reaction, and are decomposed even by carbonic acid, so as to produce mixtures of alkaline carbonate and dimetallic phosphate:—

$$Na_3PO_4 + H_2CO_3 = Na_2HPO_4 + NaHCO_3.$$

Among dimetallic phosphates, those of the alkali-metals are also soluble in water. They are often spoken of as the neutral phosphates, but their solutions have, nevertheless, a feebly alkaline reaction. The remaining dimetallic phosphates are unstable, and generally insoluble compounds, which have a strong tendency to decompose into soluble mono-metallic and insoluble trimetallic salts.

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The mono-metallic phosphates are all soluble in water, forming strongly acid solutions. Most trimetallic phosphates dissolve to a greater or less extent in aqueous phosphoric, nitric, and chlorhydric acids, with probable conversion into mono-metallic salts; but, save in a very few instances, monometallic phosphates of the heavy metals are not known as definite compounds.

Under ordinary circumstances, the heavy metals, silver and lead for instance, form only one class of orthophosphates, namely, the triphosphates, whence arises a peculiarity connected with the mutual decomposition of soluble diphosphates and silver salts, which, prior to the researches of Graham, was considered to be in the highest degree anomalous. It was ascertained by Wenzel, in 1773, and subsequently recognised as a general law, that when two neutral salts decompose one another, the products are also neutral. Thus with sulphate of sodium and nitrate of silver we have the reaction:—

$$Na_2SO_4 + 2AgNO_3 = Ag_2SO_4 + 2NaNO_3.$$

In this case, the reacting and the resulting salts are alike neutral; or the sodium displaced from its sulphate is exactly sufficient to saturate the nitric residue left by the silver, and the silver displaced from its nitrate is exactly sufficient to saturate the sulphuric residue left by the sodium. This empirical or observational law constituted one of the fundamental points from which the doctrine of combination in atomic proportions was ultimately evolved. But the only two soluble phosphates with which chemists were formerly well acquainted, namely, the diphosphate of sodium, Na_2HPO_4, and the diphosphate of sodium and ammonium, $Na(NH_4)HPO_4$, constituted exceptions to this law. Their solutions were found to be neutral or slightly alkaline, but when added to a perfectly neutral solution of nitrate of silver, mutual decomposition ensued, with the production of a yellow precipitate of phosphate of silver, and most inexplicably a strongly acid supernatant liquid. At that time polybasic acids and salts were unknown; but directly phosphoric acid was proved to be a tribasic acid capable of forming three distinct classes of salts, the above anomaly was recognised as a necessary consequence of the constitution of the diphosphates, and was shown to pertain to monophosphates also, but not to triphosphates, thus:—

$$NaH_2PO_4 + 3AgNO_3 = Ag_3PO_4 + NaNO_3 + 2HNO_3.$$
$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3.$$
$$Na_3PO_4 + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3.$$

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All orthophosphates give with silver salts, a lemon-yellow precipitate of triphosphate of silver Ag_3PO_4, soluble in ammonia and in excess of both nitric and acetic acids. They give with lead salts a white precipitate of phosphate of lead Pb_3PO_4, which fuses readily before the blowpipe, and on cooling solidifies as a semicrystalline mass: the precipitate is soluble in nitric, but insoluble in acetic acid. They give, with ferric salts, a buff-coloured precipitate of ferric phosphate $Ffe'''PO_4.2H_2O$, insoluble in acetic, but readily soluble in mineral acids. This precipitate, unless formed under special conditions, is liable to a considerable variety of composition. They give with solution of nitrate of bismuth, a white precipitate of phosphate of bismuth $Bi'''PO_4$, insoluble in dilute nitric acid. They give with ammoniacal solutions of magnesium salts, a white crystalline precipitate of phosphate of magnesium and ammonium $Mg_2(NH_4)PO_4.6H_2O$, the properties of which have been already described. When molybdate of ammonium is added to the solution of a phosphate acidulated with nitric acid, a characteristic yellow crystalline compound of phosphoric and molybdic acids with ammonia is precipitated.

The trimetallic orthophosphates of non-volatile metals can generally withstand the action of a red heat; but the mono- and di-metallic salts yield meta- and pyro-phosphates, as previously described. The triphosphates of alkali- and alkaline earth-metals are not decomposed by ignition with charcoal, but the mono- and di-phosphates are decomposed into triphosphates and phosphorus-vapour. Triphosphates of the heavy metals, however, are decomposed by ignition with charcoal, generally with transformation into metallic phosphides; but triphosphate of lead yields metallic lead and phosphorus vapour. The different phosphates of magnesium, when heated with charcoal, evolve phosphorus, and leave a residue of magnesia. Potassium or sodium, when heated with phosphates, effects a reduction of the salts and formation of a phosphide of the alkali-metal, which evolves phosphoretted hydrogen when moistened with water.

(331) *a.* Many phosphates are found native, though rarely in a state of purity. Hence the formulæ accorded to native phosphates, more particularly to somewhat complex phosphates, such as those of copper, iron, and aluminum, are given differently by different authors. Several native phosphates are found in combination with fluorides or chlorides. The *apatites*, for instance, are usually represented by the formula $3Ca_3PO_4.CaF$, and the *wagnerites* by the formula $Mg_3PO_4.MgF$, in both of which a part or all of

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the fluorine may be displaced by chlorine. By some chemists, however, the fluorine or chlorine of apatite is considered to be accidental, and variable in its proportion to such an extent that some well crystallized varieties scarcely contain a trace of halogen-salt. On the other hand, it must be remembered that similar fluor-phosphate compounds have been formed artificially, the crystallized sodium-apatite, for instance $3Na_3PO_4.NaF.12H_2O$. *Pyromorphite* $3Pb_3PO_4.PbF$, is another native fluor-phosphate, the fluorine of which is wholly or in part replaceable by chlorine. It corresponds in crystalline form and composition to apatite, and like that mineral is occasionally found quite free from any halogen-salt. Mineralogists are also acquainted with an *iron-manganese-apatite* $3Fe_2MnPO_4.FeF$, imperfectly crystallized in hexagonal prisms resembling those of common apatite and pyromorphite. *Wavellite* is essentially a hydrated basic phosphate of aluminum, generally containing also a small proportion of fluoride of aluminum. *Amblygonite* is a complex mineral of very doubtful formula, containing basic phosphate of aluminum and phosphate of lithium.

β. The phosphates of alkali-metals are usually made by treating phosphoric acid, or bi-acid phosphate of calcium, with alkaline hydrates or carbonates. Rhombic phosphate of sodium $Na_2HPO_4.12H_2O$, which is a commercial product, is made by decomposing, with carbonate of sodium, a hot solution of the biacid phosphate of calcium, resulting from the action of sulphuric acid on bone earth :—

$$2CaH_2PO_4 + 2Na_2CO_3 = 2Na_2HPO_4 + Ca_2CO_3 + H_2O + CO_2.$$

After boiling, the solution of phosphate of sodium is filtered off from the insoluble carbonate of calcium and evaporated to the crystalizing point, and the crystals are purified by solution and recrystallization. The monometallic and trimetallic phosphates of sodium are made from this salt by the addition thereto of phosphoric acid and caustic soda respectively. Diammonic phosphate is made by the same process as di-sodic phosphate, carbonate of ammonium being substituted for carbonate of sodium. The monammonic and triammonic phosphates are made by adding phosphoric acid and ammonia respectively to the diammonic compound. Microcosmic salt, $Na(NH_4)HPO_4.4H_2O$, is made by boiling together concentrated solutions of di-sodic phosphate and sal-ammoniac. Common salt remains in solution while microcosmic salt crystallises out. It is purified by solution and recrystallization :—

$$Na_2HPO_4 + NH_4Cl = Na(NH_4)HPO_4 + NaCl.$$

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The insoluble phosphates are made by precipitating soluble salts of the respective metals with alkaline phosphates.

(332) SULPHIDES OF PHOSPHORUS.—These bodies are not very generally known. There appear to be at least three definite compounds, corresponding to the formulæ P_2S, P_2S_3, and P_2S_5, respectively. A subsulphide P_4S, and a persulphide P_2S_{12}, have also been described.

Protosulphide of phosphorus P_2S, is made by dissolving one part of sulphur in two parts of phosphorus melted under hot water, and agitating the product with aqueous ammonia. It occurs as a transparent yellow oily liquid, which may be distilled without change in an atmosphere free from oxygen. At a little below zero, it solidifies into a mass of yellow interlaced crystals. It is scarcely affected by cold, but is readily decomposed by boiling water. It dissolves in basylous sulphides or sulphydrates, forming sulphypophosphites, which, like the ordinary hypophosphites, are monometallic.

The other two sulphides of phosphorus may be made by warming the protosulphide with additional proportions of sulphur. Serullas obtained the trisulphide by decomposing terchloride of phosphorus with sulphuretted hydrogen. Kekulé has shown that both the tri- and the penta-sulphide may be readily prepared by gently heating together, in an atmosphere of carbonic anhydride, the necessary proportions of sulphur and amorphous phosphorus. The reactions take place with some violence, but not with explosion.

Trisulphide of phosphorus is a yellow, readily fusible solid, which, after fusion, remains soft and translucent for some time. When distilled in an atmosphere freed from oxygen, it yields a lemon-yellow crystalline sublimate. It is decomposed by the action of moisture, and still more rapidly by alkaline solutions. With basylous sulphides or sulphydrates, it forms definite sulphophosphites, which are dimetallic. Pentasulphide of phosphorus is a pale yellow fusible solid, which, unlike the trisulphide, crystallizes readily after fusion. In the absence of oxygen, it distils without decomposition, and, if slowly volatilized, yields a sublimate of isolated transparent crystals, having only a pale yellow tint. It is decomposible by water and alkaline solutions. With basylous sulphides and sulphydrates it forms di-metallic sulphophosphates. Wurtz's sulphoxiphosphates have already been referred to, together with the sulphochloride and sulphobromide of phosphorus (vide par. 308). The formulæ of the other sulphur-salts of phosphorus

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are not well established, but they probably correspond to those of the different oxygen-salts, thus: —

Hypophosphite	$Na\ H_2PO_2$	$Na\ H_2PS_2$	Sulphypophosphite.
Phosphite	$Na_2H\ PO_3$	$Na_2H\ PS_3$	Sulphophosphite.
Phosphate	$Na_2H\ PO_4$	$Na_2H\ PS_4$	Sulphophosphate.
	$Na_3\ PO_4$	Na_3PSO_3	Sulphoxiphosphate.

Compounds of Phosphorus and Nitrogen.

(333) The ammoniacal salts of the different phosphorus-acids have been previously described. We have now to consider several more or less well-defined compounds pertaining to the triequivalent phosphoric radicle $(PO)'''$. Similar compounds of the triequivalent phosphorous radicle P''' also exist, but they have not been so accurately examined. The relations of the chlorides, hydrates, and amides of the two radicles is shown below. These bodies may be looked upon as derivatives of the triple molecules of chlorhydric acid, water, and ammonia respectively, in each of which three atoms of hydrogen have been displaced by one terequivalent atom of the radicle, thus:—

Chloride.	Hydrate.	Amide.
$P'''Cl_3$	PH'''_3O_3	$P'''H_6N_3$.
$(PO)'''Cl_3$	$(PO)'''H_3O_3$	$(PO)'''H_6N_3$.

Phospho-triamide $N_3H_6(PO)'''$, when heated, first gives up one atom of ammonia to form phosphodiamide $N_2H_3(PO)'''$, and then a second atom to form phosphomonamide $N(PO)'''$; and phosphoroso-triamide $N_3H_6(P)'''$, appears to behave in a similar manner. Phosphomonamide is capable of existing in combination with an atom of water, when it constitutes phosphamic acid NH_2PO_2, which forms definite salts of ammonium and other bases. Phospham N_2HP, may be regarded as a dehydrated form of either phosphodiamide or phosphamate of ammonium. With the exception of chloronitride of phosphorus $NPCl_2$, and chlorophosphamide $N_2H_4PCl_3$, all azotized compounds of the phosphoric radicle may be considered as phosphates of ammonium, minus water, and may be referred to multiple ammonia and hydrate of ammonium types (vide par. 222).

$N_3H_6(P)'''$	Phosphorosamide.
$N(PO)'''$	Monophosphamide.
$NPO.H_2O$	Phosphamic acid.
$N_2H_3(PO)'''$	Phosphodiamide.
N_2HP	Phospham.
$N_3H_6(PO)'''$	Phosphotriamide.

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(334) PHOSPHOROSAMIDE.—Trichloride of phosphorus absorbs three atoms of ammonia, with conversion into a white mass of sal-ammoniac and phosphorosotriamide: $Cl_3P + 6NH_3 = 3NH_4Cl + N_3H_6P'''$. This mass, when heated out of access of air, gives off ammonia and sal-ammoniac vapours, leaving a yellowish-white amorphous residue, which has been described as phosphide of nitrogen, but which, in all probability, consists of phosphorosodiamide N_2H_3P''', and phosphorosomonamide NP'''.

(335) CHLORONITRIDE OF PHOSPHORUS. *Sym.* $NPCl_2$; *p.n.* 116.—This compound may be looked upon as pentachloride of phosphorus Cl_5P, or Cl_3PCl_2, in which three monequivalent atoms of chlorine have been displaced by one terequivalent atom of nitrogen. It is formed by the action of pentachloride of phosphorus on ammonia, thus: $Cl_5P + 4NH_3 = NPCl_2 + 3NH_4Cl$. The product of the reaction is treated with ether, which dissolves the chloronitride, and, on evaporation, deposits it crystallized in rhomboidal prisms. The compound melts at 110° and boils at 240°. It volatilizes readily in the vapour of boiling water, which mode of sublimation furnishes a useful means for its purification. It is insoluble in water, soluble in alcohol, ether, and hydrocarbons. It is decomposed by caustic alkalies, with formation of phosphamic acid:—

$$NPCl_2 + 2KHO = NH_2PO_2 + 2KCl.$$

(336) MONOPHOSPHAMIDE. *Sym.* NPO; *p.n.* 61.—This body bears to oxichloride of phosphorus the same relation that the preceding compound bears to the pentachloride, thus:—

Cl_3PCl_2	Pentachloride	Cl_3PO	Oxichloride.
$NPCl_2$	Chloronitride	NPO	Monophosphamide.

It may be considered as monammonic phosphate, minus three atoms of water,

$$H_3PO_4 + NH_3 - 3H_2O = NPO;$$

or as ammonia in which three atoms of hydrogen are displaced by one atom of *phosphoryl* $N(PO)'''$. It results from the action of heat upon phosphodiamide, or phosphotriamide, thus:—

$$N_2H_3(PO)''' - NH_3 = N(PO)'''.$$
$$N_3H_6(PO)''' - 2NH_3 = N(PO)'''.$$

It is a white, amorphous, very permanent substance, which, when

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heated with caustic potash, yields phosphate of potassium and ammonia.

(337) PHOSPHAMIC ACID. *Sym.* NH_2PO_2; *p. n.* 79.—This compound contains the elements of one atom of monophosphamide, plus those of one atom of water, and consequently may be regarded as monammonic phosphate minus two atoms of water:—

$$H_3PO_4 + NH_3 - 2H_2O = NH_2PO_2.$$

It may also be looked upon as the hydrate of a chlorous ammonia, in which three atoms of hydrogen have been displaced by one of phosphoryl, $N(PO)'''\left\{\begin{matrix}H\\H\end{matrix}\right\}O$. Its formation from chloronitride of phosphorus has been above referred to. It is usually made by the action of dry ammonia upon phosphoric anhydride:—

$$P_2O_5 + 2NH_3 - H_2O = 2NH_2PO_2.$$

The action is attended with a considerable evolution of heat, and the production of a fused mass, consisting of phosphamic acid and phosphamate of ammonium, often mixed with a little red phosphorus. The mass is acted upon by cold water, the liquid filtered, and neutralized with ammonia, whereby phosphamate of ammonium is obtained $N(PO)'''\left\{\begin{matrix}H\\NH_4\end{matrix}\right\}O$. The solution of this salt gives precipitates in solutions of the heavy and alkaline earth-metals; and from the barium- or calcium-precipitates, phosphamic acid may be set free by the action of sulphuric acid. It is a semi-solid amorphous mass, readily soluble in water and alcohol. Moist phosphamic acid, when gently heated, takes up two atoms of water, and produces monammonic phosphate $(NH_4)H_2PO_4$.

When phosphamate of ammonium, or phosphoric anhydride completely saturated with ammonia, is heated in a current of dry ammoniacal gas, it gives off water, and leaves a yellowish-red insoluble residue of *phospham* N_2HP. This body constitutes the nitryl of phosphamic acid, corresponding to the nitryl of acetic acid, for instance: $C_2H_4O_2 + NH_3 - 2H_2O = C_2H_3N$. It differs in composition from phosphamate of ammonium, precisely as phosphamate of ammonium differs from diammonic phosphate, thus:—

$$H_3PO_4 + 2NH_3 - 2H_2O = N_2H_5PO_2.$$
$$NH_2PO_2 + NH_3 - 2H_2O = N_2HP.$$

Phospham, when added to fused hydrate of potassium not thoroughly dry, yields one atom of phosphate of potassium and two of ammonia.

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Gladstone, by the action of chloronitride of phosphorus upon alkalies, obtained two new acids, which he termed azophosphoric and deutazophosphoric respectively. Their formulæ were not satisfactorily established, and the latter acid is now thought to be identical with the phosphamic acid subsequently produced by Schiff, as above described. The former acid, namely, the azophosphoric, was regarded by Laurent as pyrophosphamic acid, but its constitution is very doubtful: —

$$H_4P_2O_7 + NH_3 - H_2O = NH_5P_2O_6.$$

(338) PHOSPHODIAMIDE. *Sym.* N_2H_3PO; *p. n.* 78.—When pentachloride of phosphorus is saturated with ammoniacal gas, sal-ammoniac and a compound known as *chlorophosphamide* are produced:—

$$Cl_5P + 4NH_3 = N_2H_4PCl_3 + 2NH_4Cl.$$

When this chlorophosphamide is boiled with water or caustic alkalies, it is decomposed into phosphodiamide and chlorhydric acid, or a chloride of alkali-metal:—

$$N_2H_4PCl_3 + H_2O = N_2H_3PO + 3HCl.$$

It is a white insoluble powder, which may be purified by boiling first in potash, and then in nitric acid. It may be looked upon as biammonic phosphate minus three atoms of water; or as phosphamate of ammonium minus one atom of water; or as phospham plus one atom of water:—

$$H_3PO_4 + 2NH_3 - 3H_2O = N_2H_3PO.$$

When added to fused potash, it forms one atom of phosphate of potassium, and evolves two atoms of ammonia. It is intermediate in composition between monophosphamide and phosphotriamide, and may be regarded as a diammonia N_2H_6, in which three atoms of hydrogen are displaced by one of phosphoryl $(PO)'''$:—

$N(PO)'''$	Monophosphamide.*
$N_2H_3(PO)'''$	Phosphodiamide.†
$N_3H_6(PO)'''$	Phosphotriamide.

When heated out of access of air, it breaks up into ammonia and monophosphamide.

(339) PHOSPHOTRIAMIDE. *Sym.* N_3H_6PO; *p. n.* 95.—When

* Gerhardt's biphosphamide. † Gerhardt's phosphamide.

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dry ammonia is passed into oxichloride of phosphorus, a mixture of sal-ammoniac and phosphotriamide is produced:—

$$Cl_3PO + 6NH_3 = N_3H_6PO + 3NH_4Cl.$$

The sal-ammoniac may be removed by washing with water, when the phosphotriamide is left as a white, insoluble, amorphous mass. It may be looked upon as triammonic phosphate minus three atoms of water, thus:—

$$H_3PO_4 + 3NH_3 - 3H_2O = N_3H_6PO.$$

It constitutes a variety of triammonia N_3H_9, in which three atoms of hydrogen are displaced by one atom of phosphoryl PO‴. Heated by itself, out of access of air, it gives off ammonia, to form phosphodiamide and monophosphamide successively. Heated with caustic potash, it yields one atom of phosphate of potassium and three atoms of ammonia. Like monophosphamide and phosphodiamide, it is not easily attacked by liquid reagents. It is decomposed, however, when heated with strong sulphuric acid.

Sulphosphotriamide N_3H_6PS, is obtained by treating sulphochloride of phosphorus with dry ammonia. It is a white amorphous substance, gradually decomposed by water, with evolution of sulphydric acid.

If we treble the formula of monophosphamide, it will appear as a variety of phosphotriamide, in which nine atoms of hydrogen are displaced by three atoms of phosphoryl, thus:—

Monophosphamide.		Phosphotriamide.
$\left.\begin{matrix}PO\\PO\\PO\end{matrix}\right\}N_3$	$\left.\begin{matrix}PO\\PO\\H_3\end{matrix}\right\}N_3$	$\left.\begin{matrix}PO\\H_3\\H_3\end{matrix}\right\}N_3.$

The intermediate compound is unknown. It would represent dehydrated pyrophosphate of ammonium:—

$$H_4P_2O_7 + 3NH_3 - 5H_2O = N_3H_3(PO)_2.$$

§ III. Arsenic.

Symbol As, *Proportional number*, 75; *Vapour density*, 150; *Atomic volume*, □.

(340) Arsenic is found native in the reguline state, and combined with other metals to form metallic arsenides, such as those of iron, manganese, nickel, and cobalt; also as a substitute for one-half the sulphur in metallic bisulphides, as in cobalt-glance, nickel

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glance, and mispickel. It likewise occurs in combination with sulphur, to form the bisulphide or realgar, the tersulphide or orpiment, and united with other metallic sulphides, to form numerous sulpharsenites, such as grey copper ore, tennantite, red silver, silver-copper-glance, &c. Many metallic arsenates also have been found as somewhat rare crystalline minerals. Arsenic in small quantity is very widely distributed, and presents itself as an impurity in many minerals, and in the products obtained from them. Ferruginous ores and deposits, in particular, are rarely free from traces of arsenic. The statement of Orfila, that the animal body contained arsenic as a normal constituent, proved to be unfounded. The compounds of arsenic have been known from the earliest times. They are mentioned by Dioscorides.

(341) *α.* Metallic arsenic is made by heating mispickel or arsenical pyrites in earthen tubes. The arsenic is driven off, and condenses as a grey crystalline mass in prolongations of the tubes usually made of sheet iron: $Fe_2SAs = Fe_2S + As$. This commercial arsenic may be purified by resublimation, the most volatile portions, which are more or less oxygenated, being rejected. *β.* Or the metal may be procured by reducing white arsenic or arsenious anhydride with either charcoal or black flux: $As_2O_3 + C_3 = As_2 + 3CO$. This product also may be purified by resublimation

(342) Arsenic is a brilliant, steel-grey coloured, very brittle solid, and a conductor of electricity. It crystallises in acute rhombohedrons, isomorphous with those of tellurium and antimony. Its sp. gr. varies from 5·6 to 5·9. It volatilizes at 180° and upwards, without previous fusing. It usually condenses in the crystalline form; but, according to Guy, sublimed arsenical crusts are distinctly globular or botryoidal. Arsenic vapour is colourless, and possessed of a peculiar garlic-like odour. At ordinary temperatures, the solid metal does not tarnish by exposure to dry air, but moistened pulverulent arsenic undergoes slow oxidation to form the compound known as *fly-powder*. Moreover, dry pulverulent arsenic oxidates readily at 70° and upwards. Metallic arsenic burns at a red heat with a bluish-white flame, and an abundant evolution of white smoke consisting of arsenious anhydride. It combines directly with chlorine, bromine, and iodine, the union being frequently attended with the phenomena of combustion. At a gentle heat, it also combines with sulphur to form either orpiment or realgar. It is converted into arsenic acid by treatment with hot nitric or nitromuriatic acid, and into an arsenate of alkali-metal by deflagration with nitrate of sodium or potassium. Chlorhydric acid

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has very little action upon metallic arsenic. According to Berzelius, arsenic exists in two allotropic forms, the one steel-grey, crystalline, and readily oxidizable in moist air ; the other, lustrous, tin-white, denser, and much more difficultly oxidizable. The latter variety is produced when the metal is strongly heated, or when it is condensed at a high temperature in an atmosphere of its own vapour. The arsenic produced by heating mispickel usually assumes this form, whereas that resulting from the deoxidation of white arsenic assumes the other.

(343) The ready reducibility of arsenical compounds and volatility of metallic arsenic constitute the basis of what is known as the reduction test for arsenic. When white arsenic, orpiment, Scheele's green, or other mineral compound of arsenic is mixed with four or five times its bulk of dried soda-flux*, and introduced into a narrow reduction tube of hard glass, made perfectly dry and warm, there is produced, on subjecting the mixture to the heat of a spirit flame, a sublimate of reduced arsenic, which condenses in the upper cool part of the tube in the form of a metallic ring. This arsenical ring is characterised: *α.* by its lustrous steel-grey appearance. Should it have an opaque brownish-black colour, its proper aspect may be brought out by the cautious application of heat, when the characteristic metallic grey ring will remain, and a more volatile dark-coloured compound of arsenic be volatilized. The interior surface of the metallic sublimate, rendered visible by breaking the tube, presents a crystalline appearance. *β.* By its volatility. On heating the sublimate to a temperature considerably below redness, it is readily volatilized from one part of the tube to another. *γ.* By its conversion into arsenious anhydride. After repeated volatilizations up and down the tube, the ring of metal is gradually replaced by a ring of iridescent crystals of arsenious anhydride, which may be seen by a lens to consist of octa- and tetrahedral forms. These may be boiled in a small quantity of water for some time, when a solution of arsenious acid will be formed, to which the ordinary liquid reagents can be applied. *δ.* By its conversion into arsenic acid. The ring of metal, when warmed with a drop or two of nitro-muriatic acid, disappears, and on evaporation to dryness, a residue of arsenic acid is left, which may be dissolved in water, and tested with nitrate of silver solution, whereby a brick-red precipitate of arsenate of silver will be produced.

* Procured by the incineration of acetate of sodium.

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ARSENAMINE.

Symbol H_3As; *Proportional number* 78; *Density* 39; *Atomic volume* □□.

(344) *a.* This gas, also known as arsenetted hydrogen, may be prepared by decomposing metallic arsenides with water or acids. Thus, with water and arsenide of sodium we have the reaction $3H_2O + Na_3As = 3NaHO + H_3As$. Again, when arsenide of zinc, prepared by fusing together equal weights of zinc and arsenic, is acted upon by strong chlorhydric acid, or by sulphuric acid diluted with three parts of water, we have a similar reaction, thus: $3H_2SO_4 + Zn_3As = 3ZnHSO_4 + H_3As$. *β.* Arsenetted hydrogen in greater or less amount seems also to be produced whenever arsenious or arsenic acid, or any of their salts, is in presence of nascent hydrogen: $H_3AsO_3 + H_6 = H_3As + 3H_2O$. The readiest mode of preparing arsenamine consists in acting upon metallic zinc by ordinary chlorhydric or diluted sulphuric acid in which arsenious anhydride has been dissolved, but the gas so prepared is always mixed with a considerable proportion of uncombined hydrogen. Iron and tin act much less efficiently than zinc in producing arsenetted hydrogen. The hydrogen evolved from the negative pole of a battery of several cells also reduces arsenious acid to the state of arsenamine, as shown by Bloxam; but a weak current produces only a deposit of metallic arsenic.

(345) Arsenamine is a colourless gas, having a most unpleasant odour. It is condensed at —40° into a transparent liquid which has not been solidified, although cooled to —110°. Water, at ordinary temperatures, dissolves about one-fifth of its volume of the gas. Neither the gas nor its aqueous solution has any action upon blue or red litmus paper. Arsenetted hydrogen, even when much diluted, is highly poisonous, and its accidental respiration has frequently led to fatal results. The gas is decomposed below a red heat into metallic arsenic and hydrogen. It is slowly decomposed in a similar manner by exposure to sunlight. When mixed with oxygen, and exploded by the electric spark, it forms water and arsenious anhydride, thus: $2H_3As + O_6 = As_2O_3 + 3H_2O$. Should there be a deficiency of oxygen, the hydrogen alone is oxidated into water, while metallic arsenic is deposited. Arsenetted hydrogen burns in the air with a bluish-white flame, forming water and an abundant white smoke of arsenious anhydride. When the access of air is partially cut off, by depressing the flame

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with a surface of cold porcelain for instance, the hydrogen only is burnt, while the metallic arsenic is deposited as a brilliant steel-grey mirror, which may be readily volatilized by heat. A mixture of arsenamine and oxygen gases is also decomposed by sunlight, with formation of water and deposition of arsenic; and the aqueous solution of arsenamine is decomposed by exposure to air in a similar manner. Arsenetted hydrogen gas is decomposed by hypochlorous, nitric, nitro-muriatic, and all oxygenating acids, including strong sulphuric acid. Chlorine in excess reacts violently upon it, forming trichloride of arsenic and chlorhydric acid. But when chlorine is allowed to bubble up into a jar of arsenamine, each successive bubble bursts into flame, forming chlorhydric acid and metallic arsenic. The reactions of bromine and iodine are similar to, but less violent than those of chlorine. Sulphur heated in the gas forms sulphydric acid, and either metallic arsenic or sulphide of arsenic. Phosphorus heated in the gas forms phosphamine and phosphide of arsenic. Sodium and zinc, at a moderate heat, withdraw the arsenic and set free hydrogen. Arsenetted hydrogen is decomposed by transmission over heated hydrate of sodium or potassium, with absorption of the arsenic to form metallic arsenite and arsenide, and liberation of hydrogen derived from both the gas and the hydrate. Solutions of most heavy metallic salts decompose arsenetted hydrogen, with production of water and either metallic arsenide, or arsenious acid and metal, thus:—

$$3Cu_2SO_4 + 2H_3As = 3H_2SO_4 + 2Cu_3As.$$
$$6AgNO_3 + 3H_2O + H_3As = 6HNO_3 + H_3AsO_3 + Ag_6.$$

The aqueous solution of arsenetted hydrogen gives dark coloured precipitates with most heavy metallic salts. Arsenetted hydrogen gas is absorbed by oil of turpentine, with production of a definite crystalline body.

(346) Many compounds are formed on the type of arsenamine. Thus we have numerous natural and artificial arsenides of metal, those of nickel and copper for instance, represented by the formulæ Ni_3As and Cu_3As respectively. We have also the halogen compounds of arsenic, namely, the trifluoride F_3As, trichloride Cl_3As, tribromide Br_3As, and teriodide I_3As. The hydrogen of arsenamine, moreover, has been replaced by the alcohol-radicles, methyl and ethyl, &c.; and compounds have been procured by the simultaneous substitution of both halogens and alcohol-radicles for its hydrogen. Thus we have:—

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Et_3As	Triethylarsine.
Me_3As	Trimethylarsine.
$Cl\ Me_2As$	Chloride of dimethylarsine (kakodyl).
$Cl_2Me\ As$	Bichloride of methylarsine.
Cl_3As	Trichloride of arsenic.

Arsenamine itself does not combine with acids, but its alcohol-radicle derivatives form salts analogous to those of corresponding compound ammonias. Thus we have the bromethylate of triethyl-arsine $AsEt_3EtBr$, or bromide of tetrethylarsonium, &c. Moreover, compounds of the diarsine type, H_6As_2, and of mixed amine-arsine, and phospine-arsine types, H_6NAs and H_6PAs respectively, have been obtained by Hofmann.

(347) The ready production of arsenetted hydrogen, and deposition therefrom of metallic arsenic, either by imperfect combustion or the application of extraneous heat, constitute the basis of what is known as Marsh's test for arsenic. The most convenient instrument for the performance of this test consists of the original bent tube devised by Marsh with the addition of two bulbs, one in the upper part of the long, and one in the lower part of the short limb. This shorter limb is furnished with a stop-cock, into which is screwed either a jet for burning the issuing gas, or an elbow to which a horizontal piece of glass tubing may be readily adapted. When it is intended to obtain arsenical deposits by an imperfect combustion of the arsenetted hydrogen, the mode of proceeding is as follows:—The stop-cock is removed from the apparatus, and a piece of stout glass rod dropped into the shorter limb. This should be sufficiently small to fall to the bend of the tube, but not small enough to pass into the longer limb; a glass stopper will often answer the purpose extremely well. Two or three compact lumps of metallic zinc are then let fall upon the piece of glass, the stop-cock replaced, and cold diluted sulphuric acid, in the proportion of about one part of acid to six or seven of water, poured into the longer limb; so that when the liquid is level in the two limbs, there may still remain some little free space beneath the stop-cock. The dilute acid is allowed to act upon the zinc for a few minutes, and the stop-cock then closed, whereby the shorter limb becomes gradually filled with hydrogen gas, the acid being driven up into the longer limb. The stop-cock is then opened, and the issuing hydrogen quickly inflamed. It ought to burn with a scarcely visible flame, which should not produce a deposit or even a discolouration upon a piece of clean glass or porcelain momentarily depressed upon it. As soon as all the hydrogen

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is driven out of the shorter limb by the descending acid, the stop-cock is re-closed until another accumulation of gas has taken place, which is then inflamed and examined as before. When, after several examinations, the purity of the hydrogen, and consequently of the materials used to generate it, has been satisfactorily ascertained, the arsenical liquid is introduced and the experiment repeated. The hydrogen gas subsequently evolved is contaminated to a greater or less extent with arsenetted hydrogen, and produces a metallic-looking discolouration upon paper moistened with solution of nitrate of silver. It burns with a bluish flame, and evolves an opaque white smoke consisting of arsenious anhydride. This may be tested by holding over the summit of the flame a piece of porcelain moistened with ammonio-nitrate of silver, whereby a yellow deposit of arsenite of silver will be produced; or by holding over the flame, more than once if necessary, a short wide test-tube, moistened on its interior with water, whereby a weak solution of arsenious acid will be obtained, which may be tested with sulphydric acid or other suitable reagent. When a piece of clean glass, porcelain, or talc is momentarily depressed upon the flame so as to cut off about two-thirds of its height, a dark stain or deposit is produced thereon. This deposit is constituted of three products; in the centre of metallic arsenic, in the exterior of arsenious anhydride, and in the intermediate zone of a compound considered to be a suboxide of arsenic. That the stain is really arsenical is shown by its possessing the following properties. *α.* Metallic brilliancy. The lustrous appearance of the arsenical stain is best seen on its free surface, but is recognisable through the glass. *β.* Hair-brown colour. This character appertains particularly to slight stains, and to the intermediate portions of larger stains, in which last it is best manifested by means of transmitted light. *γ.* Volatility. The arsenical stain disappears readily on the application of a heat below redness. This quality is very evident when the stain has been produced upon a thin plate of talc. During its volatilization the metallic arsenic becomes converted into arsenious anhydride. *δ.* Solubility in chloride of lime. When the arsenical stain is heated with a few drops of bleaching liquid, complete solution very speedily takes place. For the application of this test it is convenient to produce the stain on the interior of a watch glass. *ε.* Non-solubility in bisulphide of ammonium. The arsenical stain is not perceptibly affected by treatment with a drop of yellow sulphide of ammonium solution. On heating to dryness, a bright yellow stain of orpiment is produced, containing a dark nucleus of undissolved metallic arsenic (Guy). *ζ.* Conversion into arsenic acid. The

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arsenical stain disappears completely when gently warmed with a drop or two of nitro-muriatic acid. By evaporation to dryness, a slight residue of arsenic acid is left, recognisable by its ready solubility in a drop of water, so as to form a solution in which nitrate of silver produces a brickdust-red turbidity.

When it is intended to decompose the arsenetted hydrogen by extraneous heat, the mode of proceeding is as follows: — A piece of narrow hard tubing is selected, and drawn out at one end to a fine orifice. At some little distance from this end, the tube is bent downwards at a right angle, while close to the other end, a small bulb is blown, and charged with chloride of calcium in the usual manner. The bulbed end of the tube is then fitted to the elbow-piece of Marsh's apparatus, and the bent free end arranged to dip into a solution of nitrate of silver. By opening the stop-cock of the charged apparatus, before introducing the arsenical liquid, hydrogen gas is allowed to pass over the chloride of calcium, along the horizontal tube and down the vertical piece, so as to bubble up through the silver solution. During the transmission of the gas, the flame of a spirit lamp is applied to the horizontal tube; and if after some time there is not produced any deposit within the tube, or precipitate in the silver solution, the materials are considered as pure; and if the effervescence be sufficiently moderate, the arsenical liquid may then be added. The arsenetted hydrogen thereby produced is decomposed in its passage through the heated portion of the tube, and deposits a steel-grey ring of metallic arsenic at some little distance beyond the flame. This ring may be identified by its appearance, its position beyond the flame, its volatility, its conversion into arsenious anhydride by repeated sublimations, and its conversion into arsenic acid by treatment with nitro-muriatic acid. Any arsenetted hydrogen that may escape decomposition by the flame is arrested by the nitrate of silver solution with formation of a black deposit of metallic silver. On the termination of the experiment, the excess of silver may be precipitated with chlorhydric acid, and the filtrate evaporated to dryness, whereby a residue of arsenic acid will be obtained, which can be dissolved in water and tested with the usual reagents. The presence of organic matter, of oxidizing agents, and of several metallic salts, prevents to a greater or less extent the formation of arsenetted hydrogen. Organic matter, moreover, frequently produces a very inconvenient frothing. Bloxam, instead of generating the arsenetted hydrogen by means of zinc and dilute acid, employs the electrolytic method. He subjects the acidified liquid to a current produced by six of

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Grove's cells, and examines the gas evolved from the negative pole, as above described.

(348) SOLID HYDRIDE OF ARSENIC. *Sym.* H_2As?—When water is electrolysed by a powerful voltaic battery, having a rod of arsenic for its negative pole, a brown powder is formed upon the surface of the metal. The same compound is produced, to some extent, by the action of water upon arsenide of sodium or potassium. It evolves hydrogen when heated in close vessels, and burns readily when heated in air. According to Soubeiran, it is a dihydride.

ARSENIDES.

(349) The arsenides possess the characters of metallic alloys. Many of them are found native. They are readily obtained by fusing arsenic with nearly any other metal. They also result from the reduction of metallic arsenites and arsenates. The arsenides of sodium and potassium are brownish substances decomposible by water with formation of arsenetted hydrogen, solid hydride of arsenic, and free hydrogen. The majority of metallic arsenides, however, constitute hard, brittle, fusible alloys. A small proportion of arsenic is introduced into shot-metal, to prevent tailing, and so cause the production of spherical globules. Metallic arsenides, save that of antimony, which is decomposed with volatilization of arsenic, are scarcely affected by mere ignition, but in presence of air they become oxidated, usually with evolution of arsenious anhydride. The arsenide of a heavy metal, when fused with a mixture of alkaline nitrate and carbonate, yields an arsenate of alkali-metal, with complete separation of heavy metallic oxide. Chlorine and sulphur each combine with both elements of the alloys. Most arsenides of protequivalent metal may be referred to some one of three general formulæ. The arsenides pertaining to the type M_3As, may be looked upon as metal derivatives of arsenamine. They may be formed artificially by fusion, as shown in the preparation of arsenide of zinc Zn_3As, for instance. The corresponding arsenide of cupricum Cu_3As, results from passing arsenetted hydrogen through a solution of copper, or over dry chloride of copper: $H_3As + 3CuCl = Cu_3As + 3HCl$. The same compound is produced by boiling finely-divided metallic copper in a chlorhydric acid solution of arsenic (vide par. 359). A few arsenides of this class have been found native, domeykite, or arsenide of cuprosum Ccu_3As, and an arsenide of nickel Ni_3As, for example. The majority of native arsenides correspond in their formulæ to protosul-

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phides, and consequently pertain to the type M_2As, as instanced by mangan-arsenide Mn_2As, kupfer-nickel Ni_2As, smaltine Co_2As, and arsenide of iron Fe_2As, &c. Other native arsenides correspond in their formulæ to bisulphides, and consequently pertain to the type H_2As_2. Tesseral pyrites $(Co,Ni,Fe)_2As_2$, white nickel pyrites Ni_2As_2, and speiss-cobalt Co_2As_2, may be taken as examples. We have many analogous compounds in which one-half the arsenic is displaced by sulphur, as in nickel blende Ni_2AsS, cobalt-blende Co_2AsS, and arsenical iron pyrites Fe_2AsS, &c.

Halogen compounds of Arsenic.

(350) Trifluoride of Arsenic. *Sym.* F_3As; *p.n.* 94.—This fluor-derivative of arsenamine is made by heating, in a leaden retort, a mixture of finely-powdered white arsenic and fluor-spar with an excess of sulphuric acid:—

$$As_2O_3 + 6CaF + 3H_2SO_4 = 3H_2O + 2F_3As + 3Ca_2SO_4.$$

The distillate is a colourless liquid of sp. gr. 2·73. It boils at 63°, and volatilises considerably at ordinary temperatures. It is decomposed by water with formation of fluorhydric and arsenious acids. Hence glass is readily attacked by the moist though not by the dry liquid.

(351) Trichloride of Arsenic. *Sym.* Cl_3As; *p.n.* 181·5; *v.d.* 90·75; □□.—*a.* This compound is formed by acting upon finely-divided metallic arsenic with dry chlorine gas. The combination is usually attended with combustion. *β.* Or it may be made by distilling a mixture of metallic arsenic and corrosive sublimate: $6HgCl + As = 3Hg_2Cl + Cl_3As$. *γ.* It may also be produced by distilling arsenious anhydride with common salt and sulphuric acid. Small lumps of fused common salt should be added from time to time to a mixture of arsenious anhydride with a large excess of sulphuric acid:—

$$As_2O_3 + 6NaCl + 6H_2SO_4 = 3H_2O + 2Cl_3As + 6NaHSO_4.$$

Trichloride of arsenic is a dense, colourless, oily liquid, which does not solidify at −29°. Its sp. gr. at 0° is 2·205. It boils at 132°, but evolves vapours freely at ordinary temperatures. It is decomposed by an excess of water into chlorhydric acid and arsenious anhydride: $2Cl_3As + 3H_2O = 6HCl + As_2O_3$. It dissolves apparently without change in strong aqueous chlorhydric acid, but not to an unlimited extent. A similar, but more dilute solution is formed by dissolving arsenious anhydride in strong aqueous chlor-

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hydric acid; and even when a weak acid is used, the arsenic which is dissolved appears to exist in the state of trichloride. Trichloride of arsenic volatilizes readily in the vapours of chlorhydric acid; and a solution of arsenious anhydride in a considerable excess of even weak chlorhydric acid may be distilled to dryness, without leaving any arsenious anhydride behind.

One of the most convenient methods of obtaining an arsenical liquid suitable for examination by Marsh's or the sulphuretted hydrogen test, consists in acting upon the suspected substance, whether mineral or organic, with strong aqueous chlorhydric acid, and distilling to dryness. On treating the residue with more chlorhydric acid, and again distilling to dryness, the whole of the arsenic will be driven over in the distillate, and so be completely separated from any organic matter or metallic compound which might have interfered with its detection by the above-mentioned tests. Chlorhydric acid having scarcely any effect upon metallic arsenic, certain arsenides, and the native or sublimed sulphides of arsenic, the distillation process is not applicable to these bodies. Moreover, it will not serve satisfactorily to separate arsenic from antimony, bismuth, or tin, the chlorides of which volatilize under the same circumstances, although, to a much less extent.

Hot trichloride of arsenic dissolves phosphorus and sulphur freely, but deposits them again on cooling. It absorbs dry ammoniacal gas, with conversion into a white solid body, considered to be a double chloride of ammonium and arsenammonium $2NH_4Cl.NHAs'''Cl$, which may be crystallized unchanged from dilute alcohol.

Two atoms of trichloride of arsenic are capable of dissolving one atom of arsenious anhydride, and the same liquid is formed by acting upon arsenious anhydride with dry chlorhydric acid gas. When distilled until it begins to froth, there separates out on cooling a viscid semi-solid mass of oxichloride of arsenic AsClO, or rather chloride of arseniosyl (AsO)Cl. This body unites with basylous metallic chlorides to form double salts, thus $(AsO)Cl.2NH_4Cl$. A solution of chloride of arsenic in the smallest possible quantity of water, deposits after some days white needle-shaped crystals of hydrated chloride of arseniosyl $(AsO)Cl.H_2O$, termed by Wallace hydrated chlorarsenious acid.

The pentachloride of arsenic Cl_5As, corresponding to the pentachlorides of phosphorus Cl_5P, and of antimony Cl_5Sb, is unknown; as is also the oxichloride of arsenic Cl_3AsO, corresponding to the oxichloride of phosphorus Cl_3PO.

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(352) TRIBROMIDE OF ARSENIC. *Sym.* Br_3As; *p.n.* 155.—This compound is readily obtained by gradually adding finely-powdered metallic arsenic to bromine contained in a tubulated retort, the action being attended with combustion. By one or two distillations, it may be obtained quite pure as a white crystalline fibrous mass, which is very hygrometric. It melts at 20°—25°, to a pale yellow liquid, and boils at 220°. It is converted by a small quantity of water into oxibromide, and by excess of water into bromhydric acid and arsenious anhydride. Oxibromide of arsenic AsBrO, corresponds generally to the oxichloride in its properties and modes of formation.

(353) TERIODIDE OF ARSENIC. *Sym.* I_3As; *p.n.* 202.—Powdered arsenic and iodine, when gently warmed together, combine, with considerable evolution of heat. By distilling a mixture of three proportions of iodine and one of arsenic, the compound is produced in the form of a lustrous orange-brown sublimate. It dissolves in boiling water without decomposition, and on evaporating down is deposited in fine red needles. It may be readily crystallised from boiling alcohol, when it appears in the form of shining brick-red laminæ. When the hot aqueous solution of teriodide of arsenic is allowed to cool slowly, it deposits thin pearly laminæ of a peculiar hydrated oxiodide of arsenic, not corresponding to the oxibromide and oxichloride.

OXIDISED COMPOUNDS OF ARSENIC.

(354) The series of oxidised compounds of arsenamine is very imperfect of itself, though very complete if we include in it the metal- and radicle-derivatives of the different compounds, thus:—

Arsenamine .	H_3As	Me_3As	Trimethylarsine.
" .	H_3AsO	Me_2HAsO	Hydrate of kakodyl.
" .	H_3AsO_2	Me_2HAsO_2	Kakodylic acid.
Arsenious acid .	H_3AsO_3	Ag_3AsO_3	Arsenite of silver.
Arsenic acid .	H_3AsO_4	Ag_3AsO_4	Arsenate of silver.

Arsenic acid is a well-defined compound, procurable in distinct crystals. Arsenious acid is not known in the separate form, but only in the state of aqueous solution. The arsenites M_3AsO_3, and the arsenates M_3AsO_4, are tolerably well-known salts, although the arsenites have not been minutely examined. The anhydrides corresponding to the two acids are very well-known bodies.

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By their reactions with water, they produce the arsenious and arsenic acids respectively, thus: —

$$As_2O_3 + 3H_2O = 2H_3AsO_3$$
$$As_2O_5 + 3H_2O = 2H_3AsO_4$$

Arsenious acid results from the oxidation of arsenamine, and arsenic acid from the oxidation of arsenious acid. Conversely arsenious acid results from the deoxidation of arsenic acid, and arsenamine from the deoxidation of arsenious acid.

When metallic arsenic is exposed to moist air, it becomes covered with a black film, or even crumbles into a black powder, which is considered by some chemists to be a definite *suboxide of arsenic*. The same body is produced in the imperfect deoxidation of arsenious anhydride by heated charcoal, and also during the imperfect combustion of arsenamine. This suboxide of arsenic, when gently heated out of excess of air, is resolved into arsenious anhydride which sublimes, and metallic arsenic which is left. It is usually thought to be a mere mixture of the two.

Arsenious Anhydride, Acid, and Salts.

(355) Arsenious Anhydride. *Sym.* As_2O_3; *p. n.* 198; *v. d.* 198; □.—This compound, familiarly known as white arsenic, has been occasionally found native in the form of capillary crystals surrounding ores of nickel and cobalt. It results from the direct oxidation of the vapour of metallic arsenic, but is made commercially by roasting mispickel Fe_2SAs, and is also obtained as a by-product in the treatment of other arsenical ores, those of silver, tin, cobalt, and nickel, for instance. In Silesia, which furnishes the largest supply of arsenical pyrites, the powdered ore is roasted in a muffle, and the vapour so produced conducted into a large many-partitioned chamber, wherein the arsenious oxide or anhydride is deposited in the state of a fine powder, known as poison flour. It is purified by sublimation from iron pots, and recondensation in the pulverulent state. This product, resublimed at a higher temperature, and condensed in the form of a translucent glass, constitutes vitreous arsenic. Commercial white arsenic, unless purposely adulterated, is usually very pure. It may, however, if necessary, be purified by slow sublimation, when it condenses in brilliant, transparent, octahedral and tetrahedral crystals. Or it may be digested for some hours, with frequent agitation, in

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strong aqueous ammonia, heated to about 75°. The clear liquid, on cooling, then deposits octahedral crystals of the pure anhydride (Berzelius), sometimes, however, mixed with prismatic crystals of dibasic arsenite of ammonia (Bloxam).

(356) Massive white arsenic, when first produced, exists in the form of hard, translucent, or even transparent glassy lumps, often having a slight buff tint. According to Pereira, it may be preserved in this state for any length of time in sealed tubes, but by exposure to air it gradually becomes opaque and brittle, the opacity slowly proceeding from the exterior to the centre of the masses. According to some authors, the transition is accelerated by elevation of temperature, and is independent of the presence of air and moisture; while according to others, a trace at least of moisture is essential to the transformation. The transparent is at once converted into the opaque modification by mere pulverisation. The nature of the difference between the vitreous and porcelanous forms of massive white arsenic is not understood, but it seems that the specific heat of the former is greater than that of the latter variety. According to Rose, the crystals deposited on cooling a concentrated solution of the vitreous modification in boiling chlorhydric acid, have the properties of the opaque variety, and the formation of the crystals is attended with flashes of light visible in the dark; but the crystals deposited under the same circumstances from a chlorhydric acid solution of the opaque variety are formed without any luminous appearance. The opaque form of white arsenic is indeed considered by some chemists to be identical with the crystalline, and they regard the conversion of the transparent into the opaque variety, as a mere transition from the amorphous to the crystalline state.

The density of transparent arsenic is certainly greater than that of the opaque. Guibourt estimates the two specific gravities at 3·738 and 3·695 respectively; Taylor, at 3·793 and 3·529 respectively. The statements with regard to the relative solubilities of the two varieties are very contradictory. According to Bussy, both modifications may exist together in aqueous solution, but prolonged ebullition changes the opaque into the vitreous variety, while at a low temperature water converts the transparent into the opaque variety. According to Bussy, also, transparent arsenic is much more soluble in cold water than is the opaque. These statements of Bussy's are quite in accordance with the well-known fact, that opaque arsenic is scarcely soluble in cold water, but that when boiled for some time in water, a solution is formed

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which, even after cooling, retains a considerable quantity of dissolved arsenic, some portion thereof, however, being very slowly deposited. Taylor says, "Cold water allowed to stand for many hours on the poison (powdered white arsenic) does not dissolve more than from the $\frac{1}{1000}$ to the $\frac{1}{500}$ part of its weight; *i.e.* one half-grain to one grain of arsenic to nearly one fluid ounce of water. Water cooling from 212° F. on the poison in powder dissolves about $\frac{1}{100}$ part of its weight. That is in the proportion of nearly one grain and a quarter to a fluid ounce of water. Water boiled for an hour on the poison and allowed to cool holds dissolved $\frac{1}{10}$ part of its weight, or about eleven grains to one ounce." Guibourt found that an aqueous solution of the vitreous acid reddened litmus, but that that of the opaque compound not only did not redden litmus, but exhibited a slightly alkaline reaction. According to Christison, Pereira, and other observers, however, the solutions of both varieties have an acid reaction. The non-adhesion of pulverulent arsenious anhydride to water is so marked as to be almost characteristic. The powder may be violently agitated and even boiled with water without becoming thoroughly wetted; and some portion of it will almost always remain upon the surface as an opaque white scum, floated by the adherent air.

(357) Crystalline arsenious anhydride is dimorphous. When deposited from its solutions in water, chlorhydric acid, or ammonia, or when slowly sublimed, it usually crystallizes in more or less modified forms of the regular system. But it has been found native, and also obtained artificially, both by solution and sublimation, in rhombic prisms belonging to the right prismatic system, and isomorphous with those of teroxide of antimony in its common form. When powdered white arsenic is heated under pressure, it fuses, and on cooling solidifies into a transparent glass; but ordinarily it softens at about 200°, and volatilizes without fusing, yielding a colourless and inodorous vapour of anomalous density. This vapour may be condensed as a sublimate of transparent, iridescent, but otherwise colourless crystals, the triangular facets of whose octahedral and tetrahedral forms are easily recognised by microscopic examination. Vitreous white arsenic may be fused even at ordinary pressures without any considerable volatilization.

Arsenious anhydride is reduced at a dull red heat by carbon, hydrogen, and many of the metals. When distilled with an alkaline acetate, it yields kakodyl C_2H_6As, recognizable by its peculiar intolerable odour. By treatment with chlorine-water, hypochlorous acid, nitro-muriatic acid, or nitric acid, it is converted by oxidation

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into arsenic acid. It dissolves in solutions of hydrated and carbonated alkali, forming arsenites of the alkali-metals. It dissolves in hot dilute acids to a greater extent than in water, but separates out more or less completely on cooling. It is nearly insoluble in alcohol, quite insoluble in ether. It dissolves readily in sulphide of ammonium solution, and on evaporation to dryness an orange-yellow residue of trisulphide of arsenic is left. Arsenious anhydride is used in the manufacture of flint glass as an oxidizing agent, to convert the ferrous into ferric compounds, and thereby prevent the occurrence of any green tinge in the product.

Although the chemical functions of teroxide of arsenic are rather acidulous than basylous, yet the compound is capable under certain circumstances of acting as a base, apparently much in the same manner as the sesquioxide of uranium. Thus we are acquainted with a chloride of arseniosyl $(AsO)Cl$, analogous to chloride of uranyl $(U_2O)Cl$; a hydrated tartrate of arseniosyl and potassium $C_4H_4K(AsO)O_6.H_2O$, analogous to tartar-emetic $C_4H_4K(SbO)O_6.H_2O$; and an anhydrous sulphate of arseniosyl, probably $(AsO)_2SO_4$.

(358) ARSENIOUS ACID. *Sym.* H_3AsO_3; *p.n.* 126.—This acid is not known in the isolated form, but only in the state of aqueous solution. The solution procured by boiling an excess of white arsenic in water for some time, and then cooling, is a clear, colourless, inodorous liquid, having a slightly styptic taste, and a decided acid reaction. It neutralises alkaline hydrates, and at a boiling heat, decomposes metallic carbonates with effervescence. When evaporated down almost to dryness, it deposits octahedral crystals of arsenious anhydride.

Aqueous arsenious acid acts as a slow reducing agent. By exposure to air it gradually absorbs oxygen, with conversion into arsenic acid. It decolourises solutions of bromine and iodine, turns the orange colour of chromic acid to green, renders the red solution of permanganic acid brown and finally colourless, and reduces the salts of gold to the metallic state. When iodine, or chlorine with iodide of potassium, is added to a solution of arsenious acid mixed with a little starch paste, the whole of the arsenious acid has to be oxidized into arsenic acid before any purpling of the starch can be effected. Arsenious acid added to an excess of lime-water produces a white precipitate of arsenite of calcium. It has no effect upon solutions of sulphate of copper and nitrate of silver until neutralised by an alkali, but gives with ammonio-sulphate of copper an apple-green precipitate of arsenite of copper Cu_3AsO_3, and with ammonio-nitrate of silver a yellow precipitate of arsenite

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of silver Ag_3AsO_3. Sulphuretted hydrogen gas produces a yellow discolouration in aqueous arsenious acid, but does not throw down a precipitate until after the addition of some stronger acid (vide par. 366). After acidification with chlorhydric acid, it will produce a yellow precipitate of orpiment As_2S_3, in a solution of one part of arsenious anhydride in 80,000 parts of liquid (Lassaigne). Aqueous arsenious acid when electrolysed by a weak current yields a deposit of metallic arsenic upon the negative pole; but when electrolysed by a powerful current, or acted upon by zinc and dilute sulphuric or chlorhydric acid, it evolves arsenetted hydrogen.

(359) When a piece of clean metallic copper is boiled in even a very dilute solution of arsenious acid acidulated with chlorhydric acid, a steel-grey deposit is formed upon the surface of the copper. This reaction, which was introduced by Reinsch in 1841, constitutes the basis of what is now well known as Reinsch's process for the detection of arsenic. Assuming that the chlorhydric acid solution of arsenious acid actually contains chloride of arsenic, though a parallel explanation may be given on the assumption of its containing unaltered arsenious acid, we have the following reaction:—

$$Cl_3As + Cu_6 = 3CuCl + Cu_3As.$$

The chloride of copper remains in solution, while the steel-grey arsenide of cupricum forms a coating upon the surface of the metallic copper. When the coated copper is heated in a reduction tube, the arsenide of cupricum is decomposed with volatilization of one half its arsenic, which, becoming oxidated into arsenious anhydride, is deposited on the cool part of the tube in the form of brilliant crystals, characterised by their triangular facets. The other half of the arsenic remains in the state of arsenide of cuprosum, thus:—

$$4Cu_3As + O_3 = As_2O_3 + 2Cu_6As, \text{ or } 2Ccu_3As.$$

The crystalline sublimate may be dissolved in water, and the solution so formed examined by any of the usual reagents; or it may be converted into orpiment by the action of sulphide of ammonium, or into arsenic acid by treatment with a few drops of nitric or nitro-muriatic acid, and evaporation to dryness. The mere production of the grey deposit on copper is of itself fallacious, inasmuch as the chlorhydric acid solutions of many metals yield

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deposits upon copper resembling more or less closely that produced by arsenic; but the formation of a steel-grey deposit convertible into a crystalline sublimate, and this again into orpiment, or yellow arsenite, or red arsenate of silver, is quite characteristic of the poison. The presence of organic matter does not interfere in any way with Reinsch's process, hence its great use in toxicological inquiries. Its delicacy is, moreover, very great. One thousand grains, or rather more than two fluid ounces of dilute chlorhydric acid, holding dissolved $\frac{1}{1000}$ of a grain of arsenious anhydride, will give consecutively a steel-grey deposit, a crystalline sublimate, and a coloured residue of orpiment or arsenate of silver.

Reinsch's process, being essentially a process of reduction, is not applicable in the presence of oxidizing agents, which, moreover, enable dilute chlorhydric acid to dissolve metallic copper. Any oxidizing agent, however, may be readily reduced by acid sulphite of sodium, and the excess of sulphurous acid driven off, before introducing the copper. Inasmuch as Reinsch's process necessarily involves the solution of a minute quantity of copper, and as commercial copper is very liable to contain arsenic, it should always be submitted to examination before being used. In the ordinary mode of experimenting, the quantity of copper dissolved is almost inappreciable, so that if a solution of four or five grains of the copper to be employed does not yield any trace of arsenic, it is quite pure enough for the purpose.

(360) Arsenites.—Arsenious anhydride apparently unites with bases in three different proportions to form mono-metallic, di-metallic, and tri-metallic salts, represented respectively by the general formulæ MH_2AsO_3, M_2HAsO_3, and M_3AsO_3. It seems also to form metasalts $MAsO_2$, and parasalts $M_4As_2O_5$, or $M_3AsO_3.MAsO_2$. The arsenites are for the most part somewhat unstable, and have not been minutely examined. The arsenites of the alkali-metals and ammonium are soluble in water, and even crystallizable, though with difficulty. Their solutions are decomposed at ordinary temperatures by the carbonic acid of the air. The hydrates of calcium, strontium, and barium, when added to excess of aqueous arsenious acid gently heated, do not give rise to precipitates, but when aqueous arsenious acid is added to an excess of hot or cold lime, strontia, or baryta-water, insoluble arsenites are precipitated, which, however, dissolve in dilute acids and in ammoniacal salts. The other arsenites are insoluble, and procurable by double decomposition, thus :—

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$$H_3AsO_3 + 3NH_3 + 3AgNO_3 = Ag_3AsO_3 + 3NH_4NO_3.$$

Most arsenites are decomposed by heat. Those of the heavy metals yield arsenious anhydride and metallic oxide, thus:— $2Cu_3AsO_3 = 3Cu_2O + As_2O_3$; but arsenite of silver, when strongly heated, leaves a residue of metallic silver; and arsenite of lead is not decomposed. The arsenites of the alkali- and alkaline-earth metals yield arsenates and evolve metallic arsenic, thus:—

$$5K_2HAsO_3 = 3K_3AsO_4 + As_2 + KHO + 2H_2O.$$

Arsenite of silver Ag_3AsO_3, is interesting from its yellow colour, so that its production serves as a test for arsenious acid. Arsenite of copper Cu_3AsO_3, or possibly Cu_2HAsO_3, is well known in commerce as Scheele's green, and constitutes a very valuable pigment. Its formation also serves as a test for arsenious acid. Aqueous arsenite of potassium, probably KH_2AsO_3, made by dissolving arsenious anhydride in a boiling solution of carbonate of potassium, is largely used in medicine, under the name of Fowler's solution, for the treatment of ague and skin diseases.

Arsenic Anhydride, Acid, and Salts.

(361) Arsenic Anhydride. *Sym.* As_2O_5; *p. n.* 230.—This body is obtained by heating any form of arsenic acid to dull redness: $2H_3AsO_4 - 3H_2O = As_2O_5$. It is a white amorphous mass, scarcely soluble in water, and having no action upon litmus. By continued exposure to moist air it is partly converted into arsenic acid, and simultaneously becomes deliquescent. At a full red heat it is decomposed into arsenious anhydride and free oxygen. Like arsenious anhydride, it is reduced to the metallic state when heated with charcoal, cyanide of potassium, &c.

(362) Arsenic Acid. *Sym.* H_3AsO_4; *p. n.* 142.—This acid is produced by oxidizing arsenious acid or anhydride, usually with nitric, or nitro-muriatic acid, and evaporating the liquid product to a syrupy condition. After standing for some days at ordinary temperatures, this syrupy liquid deposits hydrated crystals $2H_3AsO_4.H_2O$, in the form of long prisms or rhombic laminæ. These, when heated to 100°, first melt, and then deposit the dry acid H_3AsO_4, as a crystalline precipitate. When a concentrated aqueous solution of arsenic acid is submitted to a very low temperature also, the solid acid H_3AsO_4, separates out in large prismatic crystals.

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Dry arsenic acid dissolves in water without any marked alteration of temperature, but the solution of the hydrated crystals is attended with a considerable production of cold. Aqueous arsenic acid has a sour metallic taste, and strong acid reaction. The concentrated liquid is highly corrosive, and produces painful blisters on the skin. At increased temperatures, it expels all the more volatile acids from their salts.

Arsenic acid is readily reduced to the state of arsenious acid, and consequently acts as an oxidizing agent. Thus a current of sulphurous acid, passed into a solution of arsenic acid, is oxidized into sulphuric acid, while the arsenic acid is sumultaneously reduced :—

$$H_2SO_3 + H_3AsO_4 = H_2SO_4 + H_3AsO_3.$$

When boiled with strong chlorhydric acid, arsenic acid produces trichloride of arsenic and free chlorine :—

$$H_3AsO_4 + 5HCl = 4H_2O + Cl_3As + Cl_2.$$

Sulphuretted hydrogen passed into a not too concentrated solution of arsenic acid, produces no precipitate at first, but after some time a turbidity is formed, and by continuing the passage of the gas the whole of the arsenic may be thrown down. The precipitate finally produced is usually regarded as pentasulphide of arsenic As_2S_5, but it seems to be a mere mixture of one atom of the trisulphide As_2S_3, with two atoms of sulphur S_2. The same precipitate is produced by adding thiosulphate of sodium to a solution of arsenic acid mixed with chlorhydric acid :—

$$2H_3AsO_4 + 5Na_2S_2O_3 = As_2S_5 + 5Na_2SO_4 + 3H_2O.$$

Aqueous arsenic acid gives, with nitrate of silver solution, though more readily after neutralization, a characteristic brick-red precipitate of arsenate of silver. It does not disturb a solution of sulphate of copper, but with that of the ammonio-sulphate it produces a bluish precipitate of dicupric arsenate, which, however, is not characteristic.

Arsenic acid, when tested by Reinsch's and Marsh's processes, affords much less satisfactory results than does arsenious acid; indeed, it is always advisable to reduce it to this form, by means of sulphurous acid, before applying either of the tests. Solution of arsenic acid is said to dissolve zinc and iron with liberation of pure hydrogen, but in the presence of sulphuric or chlorhydric acid some arsenetted hydrogen is always evolved.

Arsenic acid is highly poisonous, though seemingly to a less

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degree than arsenious acid or anhydride. It is used in calico-printing to discharge patterns printed with it upon a coloured ground, by an immersion of the calico in the bleaching vat.

(363) The arsenic acids corresponding respectively to metaphosphoric and pyrophosphoric acid are very unstable compounds. They dissolve in water with considerable evolution of heat, and the resulting solutions are undistinguishable from that of common arsenic acid. Metarsenic acid $HAsO_3$, is formed by gradually heating common arsenic acid to a temperature of 200°—205°. The mass becomes suddenly pasty, gives off a large quantity of aqueous vapour, and leaves a white nacreous residue, consisting almost entirely of metarsenic acid. Corresponding salts are made by heating the mono-metallic salts of common arsenic acid. Thus monopotassic arsenate KH_2AsO_4, when heated to dull redness, gives off water, and is converted into a thin liquid, which on cooling solidifies into a white mass of metarsenate of potassium $KAsO_3$. Pararsenic acid $H_4As_2O_7$, or $H_3AsO_4.HAsO_3$, is made by heating the hydrated crystals of common arsenic acid to about 150°, when pararsenic acid separates out from the dense mother liquor in the form of hard shining crystals. Corresponding salts are formed by igniting common arsenates having two atoms of fixed metal and one of hydrogen or ammonium. Thus the arsenate of magnesium and ammonium $Mg_2NH_4AsO_4$, when heated to dull redness, gives off water and ammonia, and leaves a residue of pararsenate of magnesium:—

$$2Mg_2NH_4AsO_4 = Mg_4As_2O_7 + H_2O + 2NH_3.$$

Metarsenates and pararsenates are converted respectively into monometallic and dimetallic common arsenates by the action of water.

(364) ARSENATES.—These salts correspond closely to the orthophosphates, with which they are generally isomorphous. We have monometallic, dimetallic, and trimetallic compounds represented respectively by the formulæ MH_2AsO_4, M_2HAsO_4, and M_3AsO_4. The monometallic salts, like their corresponding orthophosphates, are all soluble in water, and have an acid reaction. Of dimetallic or neutral, and trimetallic or basic arsenates, those of the alkali-metals are alone soluble in water, and their solutions have a more or less decided alkaline reaction. The dimetallic arsenates of barium, strontium, and calcium, though insoluble in water, are soluble in solutions of ammoniacal salts. Most arsenates are precipitated by double decomposition. Owing to the tendency of the heavy metals to form trimetallic arsenates, the precipitation of their salts,

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by means of neutral arsenates of alkali-metal, is often attended with the production of an acid liquid, as happens in the corresponding orthophosphate decompositions :—

$$Na_2HAsO_4 + 3AgNO_3 = Ag_3AsO_4 + 2NaNO_3 + HNO_3.$$

The arsenate of silver so produced is a brick-red precipitate. Dicupric arsenate Cu_2HAsO_4, is a pale-blue precipitate formed under similar circumstances. Triplumbic arsenate Pb_3PO_4, is a white precipitate also formed by double decomposition. When heated upon charcoal, in the reducing blowpipe flame, it fuses, and emits the characteristic smell of arsenic vapour. Arsenate of magnesium and ammonium $Mg_2NH_4AsO_4.6H_2O$, which is a crystalline precipitate, isomorphous with triple phosphate, is procured by adding arsenic acid or an alkaline arsenate to the ammoniacal solution of a magnesian salt. The various arsenates of alkali-metal correspond exactly with the similar orthophosphates in water of hydration and crystalline form. They are made by adding aqueous arsenic acid to hydrated or carbonated alkali, or by fusing arsenic acid with carbonated alkali, or by deflagrating arsenious anhydride with potash-, or soda-nitre.

The best defined native arsenates are mimetene $3Pb_3AsO_4.PbCl$, corresponding to pyromorphite $3Pb_3PO_4$. PbF ; haidingerite Ca_2HAsO_4 . H_2O; pharmacolite Ca_2HAsO_4 . $2H_2O$; olivenite Cu_3AsO_4 . CuHO; euchroite Cu_3AsO_4 . CuHO . $3H_2O$; aphanase Ccu_3AsO_4 . H_2O; erinite Ccu_3AsO_4. $6H_2O$; scorodite $FfeAsO_4$. $2H_2O$; sideretine $FfeAsO_4$. $FfeHO_2$. $6H_2O$; nickel ochre Ni_3AsO_4 . $4H_2O$; and erythrine Co_3AsO_4 . $4H_2O$.

The arsenates, when heated with charcoal, either evolve arsenic or form metallic arsenides. As a rule, the trimetallic arsenates withstand the simple action of a red heat, but most of the di- and monometallic compounds give off arsenious anhydride and oxygen.

The solution of an arsenate in dilute chlorhydric acid behaves like a mere solution of arsenic acid when treated with thiosulphite of sodium, and also with sulphuretted hydrogen, unless, indeed, the basic metal of the arsenate is also precipitable therewith, when a sulpharsenate is formed, thus :—

$$Pb_3AsO_4 + 4H_2S = Pb_3AsS_4 + 4H_2O.$$

Solutions of arsenates, acidified with nitric acid, and added to molybdate of ammonium, produce a bright yellow precipitate of arseno-molybdate of ammonium, especially on gently warming.

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Compounds of Arsenic and Sulphur.

(365) Disulphide of Arsenic.—*Sym.* As_2S_2; *p.n.* 214.—This compound, better known as realgar, has no definite oxygen analogue. It may be regarded as the arsenic representative of bisulphide of nitrogen N_2S_2. It is found native, crystallized in orange-red oblique rhombic prisms. *α.* It may be made by fusing arsenic with sulphur or with trisulphide of arsenic; but is usually obtained by heating sulphur with arsenious anhydride:—

$$S_7 + 2As_2O_3 = 3SO_2 + 2As_2S_2.$$

β. It is also prepared on the large scale by distilling common iron pyrites with arsenical pyrites:—

$$2Fe_2S_2 + 2Fe_2AsS = 4Fe_2S + As_2S_2.$$

The native crystals of realgar have a resinous lustre, and are more or less translucent. They are easily sectile, have an irregular conchoidal fracture, and give an orange-red streak upon paper. Their sp. gr. is from 3·4 to 3·6. The artificial compound occurs as a ruby-red transparent solid. Realgar is easily fusible, and on cooling solidifies as a crystalline mass. When heated in close vessels, it volatilizes after fusion, and condenses unchanged as a brittle, transparent, bright red sublimate. When heated in the air, it takes fire, burns with a blue flame, and evolves fumes of sulphurous and arsenious anhydrides. When deflagrated with nitre, it yields a brilliant white light, and leaves a residue of sulphate and arsenate of potassium. The so-called *Indian fire* is a mixture of nitre, sulphur, and realgar. When heated with black flux, it yields a sublimate of metallic arsenic. Disulphide of arsenic is insoluble in water, and is scarcely affected by chlorhydric acid. Heated with strong sulphuric acid, it forms water and sulphurous and arsenious anhydrides. It is readily attacked by nitric or nitro-muriatic acid, with conversion into sulphuric and arsenic acids. When in the finely-powdered state it is dissolved, in great part, by caustic potash or soda, an insoluble brown powder, however, said to have the formula $As_{12}S$, being left. It dissolves readily in solutions of the alkaline sulphides, with formation of sulpho-salts of very uncertain composition. The so-called hyposulpharsenites of sodium and potassium are insoluble brown powders, resulting from the spontaneous decomposition of concentrated sulpharsenite solutions (vide par. 366). The potassium

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salt is represented by the formula K_2AsS_2, or $2K_2S.As_2S_2$? Commercial realgar is an opaque, amorphous, dull red substance, usually contaminated with arsenious anhydride.

(366) TRISULPHIDE OF ARSENIC. *Sym.* As_2S_3; *p. n.* 246. — *a.* This compound, also known as arsenious sulphide, and familiarly as orpiment, occurs native in crystals isomorphous with those of realgar. They are translucent and lustrous, have a bright yellow colour, and split readily into flexible laminæ. Their sp. gr. is from 3·4 to 3·5. Their streak is lemon-yellow. *β.* Trisulphide of arsenic, in a state of purity, is made by passing a current of sulphuretted hydrogen gas into a solution of arsenious anhydride in dilute chlorhydric acid. It occurs as a brilliant yellow amorphous powder, becoming darker by heat. *γ.* An impure orpiment is made by subliming a mixture of arsenious anhydride and sulphur: it constitutes the pigment known as *King's yellow*, and always contains a considerable proportion of unaltered arsenious anhydride: —

$$S_9 + 2As_2O_3 + xAs_2O_3 = 3SO_2 + (2As_2S_3 + xAs_2O_3).$$

Arsenious sulphide melts easily, and at a higher temperature volatilizes unchanged in close vessels. Heated in the air, it burns with a pale blue flame. When deflagrated with nitre, it leaves a residue of arsenate and sulphate of potassium. Heated with carbonate of potassium or sodium in a glass tube, it yields a mirror of arsenic and a residue of arsenate and sulpharsenate of alkali-metal; but if the alkaline carbonate be mixed with charcoal or cyanide of potassium, the whole, or very nearly the whole, of the arsenic is driven off in the metallic state. The respective actions of chlorhydric, sulphuric, nitric, and nitromuriatic acids upon orpiment, resemble closely those of the same acids upon realgar.

Orpiment is apparently quite insoluble in cold water; but when freshly precipitated, it dissolves to a considerable extent in boiling water, with evolution of sulphuretted hydrogen, and formation of a colourless or pale yellow solution, which, when first produced, gives a yellow precipitate on the addition of chlorhydric acid, but after prolonged boiling is unaffected thereby. Freshly precipitated orpiment is also decomposed at a boiling heat, with a similar evolution of sulphuretted hydrogen, by dilute chlorhydric acid, though much less readily than by pure water. The above-described behaviour of trisulphide of arsenic with water may be contrasted with that of teroxide of arsenic with sulphydric acid.

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When sulphuretted hydrogen is passed into an aqueous solution of arsenious acid, there is no precipitate produced. The liquid assumes a yellow colour, but does not acquire any odour of the gas, unless it has been employed in excess. The addition of a little chlorhydric acid, however, at once throws down a precipitate of arsenious sulphide. Even with an acidulated solution of arsenious acid, moreover, provided it be very dilute, an excess of sulphydric acid will fail to throw down the whole of the arsenic, but will form a pale-coloured solution, gradually decomposed by exposure to air, with evolution of sulphuretted hydrogen and precipitation of orpiment.

It would appear that trisulphide of arsenic can react with sulphuretted hydrogen to form sulpharsenious acid H_3AsS_3, which compound exists in the solution produced by passing sulphydric acid into aqueous arsenious acid. On boiling arsenious sulphide with water, this sulpho-acid seems also to be formed in solution, together with arsenious acid, thus: —

$$As_2S_3 + 3H_2O = H_3AsS_3 + H_3AsO_3.$$

This solution of sulpharsenious acid is then gradually decomposed by further ebullition, into arsenious acid and sulphuretted hydrogen; or it may be decomposed at once by the addition of chlorhydric acid, into water and trisulphide of arsenic.

Arsenious sulphide dissolves readily in solutions of caustic alkali, with formation of an arsenite and sulpharsenite, thus: —

$$As_2S_3 + 4KHO = K_2HAsO_3 + K_2HAsS_3 + H_2O.$$

On the addition of an acid, the whole of the trisulphide of arsenic is reprecipitated, without any evolution of sulphydric acid: —

$$K_2HAsO_3 + K_2HAsS_3 + 4HCl = 3H_2O + As_2S_3 + 4KCl.$$

Arsenious sulphide dissolves to a considerable extent, when boiled in a moderately strong solution of an alkaline carbonate. The clear filtrate deposits on cooling a brown powder, said to result from the decomposition of the sulpharsenite first formed into a hyposulpharsenite which is precipitated, and a sulpharsenate which remains in solution. But the precipitate may possibly be an analogue of antimonial kermes (vide par. 387). Recently precipitated trisulphide of arsenic dissolves in solution of acid sulphite of potassium. On boiling the liquid, sulphurous anhydride is evolved, and free sulphur deposited, while thiosulphate and arsenite of potassium remain in solution (Bunsen): —

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$$2As_2S_3 + 16KHSO_3 = 6K_2S_2O_3 + 4KH_2AsO_3 + 4H_2O + 7SO_2 + S_3.$$

The production of arsenious sulphide is frequently employed as a test for the presence of arsenic. Sulphuretted hydrogen will give a yellow precipitate in an acidulated solution containing only $\frac{1}{100000}$ part of arsenious anhydride. It is characterized by its insolubility in concentrated chlorhydric acid, and by its solubility in aqueous carbonate of ammonium or acid sulphite of potassium, in each of which properties it differs from the yellow sulphides of cadmium and tin, and from the orange sulphide of antimony. Moreover, the collected precipitate may be heated with black flux in a reduction tube, when it will yield a sublimate of metallic arsenic; or it may be deflagrated with nitre, when it will leave a residue containing arsenate of potassium, which by its reaction with nitrate of silver solution, will produce a brick-red precipitate of arsenate of silver.

(367) SULPHARSENITES.—At the time when these salts were examined by Berzelius, the constitution of the arsenites and phosphites, with which they had to be compared, was very imperfectly understood, so that his results seem now to require a fresh interpretation. The ratio of arsenic to basic metal in the sulpharsenites is as one atom to one atom, one atom to two atoms, and one atom to three atoms; and the general formulæ of the salts are in all probability MH_2AsS_3, M_2HAsS_3, and M_3AsS_3 respectively.

The dimetallic salts are the most common. Those of the alkali- and alkaline-earth metals are soluble in water, and are best made by dissolving arsenious sulphide in aqueous sulphydrates:—

$$As_2S_3 + 4KHS = 2K_2HAsS_3 + H_2S.$$

The solutions of these salts have a yellowish colour and a nauseous bitter taste. They cannot be concentrated without undergoing a decomposition into an insoluble brown hyposulpharsenite, and a soluble sulpharsenate. On adding alcohol to the solution of a dimetallic sulpharsenite, a trimetallic salt is usually precipitated, and a monometallic salt left in solution:—

$$2K_2HAsS_3 = K_3AsS_3 + KH_2AsS_3;$$

but the trimetallic salt soon undergoes decomposition into hyposulpharsenite and sulpharsenate.

The insoluble sulpharsenites are usually made by precipitating some soluble salt of a heavy metal with an alkaline sulpharsenite:—

$$K_2HAsS_3 + 2CuCl = Cu_2HAsS_3 + 2KCl.$$

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Moreover, sulpharsenites result from heating certain sulpharsenates out of contact with air. Some of these seem to constitute what may be called metasulpharsenates $KAsS_2$, or $KH_2AsS_3 - H_2S$; and parasulpharsenates $K_4As_2S_5$, or $2K_2HAsS_3 - H_2S$.

Proustite is a native trimetallic sulpharsenite of silver Ag_3AsS_3, also known as light red silver. Tennantite is a trimetallic sulpharsenite of cuprosum Ccu_3AsS_3, in which a portion of the cuprosum is displaced by iron. Light grey copper is a variety of tennantite in which a portion of the cuprosum is displaced by zinc as well as iron, and a portion of the arsenic by antimony.

(368) PENTASULPHIDE OF ARSENIC. *Sym.* As_2O_5; *p.n.* 230.—This compound may be made by heating orpiment with sulphur, or by fusing the precipitate produced by sulphuretted hydrogen in a solution of arsenic acid. The aqueous acid, when treated with the gas, is at first reduced to the state of arsenious acid, with separation of sulphur, which remains for a long time suspended in the liquid:—

$$H_3AsO_4 + H_2S = H_3AsO_3 + H_2O + S.$$

The further action of the gas produces a deposit of orpiment, and so on; the depositions of sulphur and orpiment proceeding alternately. The precipitate finally produced has the composition of pentasulphide of arsenic, but is in reality a mixture of orpiment and sulphur, separable by means of dilute ammonia, which dissolves the former and leaves the latter unaffected. The precipitate produced by the addition of any acid to an aqueous sulpharsenate seems also to be a mixture of orpiment and sulphur. Pentasulphide of arsenic has a yellow colour, is easily fusible, and may be sublimed without change in close vessels. It dissolves readily in solutions of alkaline hydrates and sulphydrates.

(369) SULPHARSENATES.—These salts are mono-, di-, and trimetallic, and are represented by the general formulæ MH_2AsS_4, M_2HAsS_4, and M_3AsS_4, respectively. The sulpharsenates of the alkali-metals are soluble in water, forming pale yellow liquids, which may be prepared directly by passing sulphuretted hydrogen gas through solutions of the corresponding oxygen-arsenates:—

$$Na_2HAsO_4 + 4H_2S = Na_2HAsS_4 + 4H_2O.$$

From solutions of the dimetallic compounds, alcohol precipitates a trimetallic salt, while a monometallic salt remains in solution. The trimetallic sulpharsenates of fixed alkali may also be readily obtained by fusing mixtures of orpiment, sulphur, and alkaline

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hydrate or carbonate. The insoluble sulpharsenates are formed by double decomposition of the alkaline sulpharsenates with solutions of other metallic salts:—

$$Na_3AsS_4 + 3AgNO_3 = Ag_3AsS_4 + 3NaNO_3.$$

The sulpharsenates of alkali-metal have a lemon-yellow colour and an intensely bitter hepatic taste. The trimetallic salts are indistinctly crystalline; the di- and monometallic salts amorphous. The trimetallic alkaline salts may be heated to full redness in close vessels without alteration; but the di- and monometallic salts give off sulphur, with conversion into sulpharsenites belonging to the para- and meta- varieties. The alkaline sulpharsenates are decomposed by any acid, even the carbonic, with evolution of sulphuretted hydrogen. Their solutions undergo a complex decomposition by exposure to air. The sulpharsenate of silver is not affected by a red heat, and that of mercuricum sublimes unchanged. Most other insoluble sulpharsenates are decomposed by ignition.

§ IV. Antimony.

Symbol, Sb; *Proportional number*, 120.

(370) Antimony is found native, and also alloyed with other metals, silver and nickel for instance. The native teroxide Sb_2O_3, constitutes antimony bloom, or valentinite; and the native tetroxide Sb_2O_4, antimony ochre, or cervantite; but by far the most important ore is the trisulphide Sb_2S_3, which is known as grey antimony, or stibnite. Very many sulphantimonites are also found native.

a. In this country, antimony is usually obtained by what is termed the martial process. The sulphide is separated from its gangue by fusion, and a bundle of scrap iron, tin plate clippings, &c., thrust into the melted mass, whereby the sulphur is transferred from the antimony to the iron, and a slag of sulphide of iron formed, which floats upon the melted antimony:—

$$Sb_2S_3 + Fe_6 = 3Fe_2S + Sb_2.$$

β. Sulphide of antimony, separated from its gangue, is reduced to a coarse powder, and heated in a reverberatory furnace. By this means the greater part of the sulphur is burnt off, and a residue consisting principally of teroxide of antimony left. This residue is mixed with water, charcoal, and carbonate of sodium, into a paste, which is heated in crucibles to full redness. The antimony, as it is reduced by the charcoal, sinks to the bottom, while over it

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a slag is formed consisting chiefly of sulphantimonite of sodium. During the roasting of the trisulphide, a considerable proportion of antimony is volatilized along with the sulphur and arsenic.

Commercial antimony may be purified, by the following process, from all the metals with which it is ordinarily contaminated, with the single exception of lead. The powdered metal, mixed with about $\frac{1}{6}$ of its weight of carbonate of sodium and $\frac{1}{16}$ of its weight of sulphide of antimony, is run down in a Hessian crucible. The resulting metal is again pulverized, mixed with carbonate of sodium only, and fluxed; and this treatment may be repeated a second time with carbonate of sodium to which a little nitre has been added. The sulphide of antimony converts the foreign metals, except lead, into sulphides, which dissolve in the slag; while the arsenic is afterwards more completely separated by the alkaline carbonate in the form of arsenate of sodium.

γ. For experimental purposes, antimony may be prepared by heating to bright redness a mixture of tartar emetic and alkaline carbonate, or of basic oxichloride of antimony and black flux. The resulting metal may be re-melted with carbonate of sodium containing a little nitre.

The presence of antimony in any compound is often ascertained by mixing it with cyanide flux, and heating the mixture on a charcoal support in the blowpipe-flame. A globule of metal is produced, with an evolution of white fumes which form an abundant bluish-white incrustation upon the charcoal. That the globule consists of antimony, is shown by its brittleness and by its behaviour with nitric and nitro-muriatic acids (vide infra). Should the heat be very prolonged, the globule of metal may be entirely dissipated.

(371) Antimony is a very brittle metal, having a bluish-white colour, a brilliant metallic lustre, and a highly crystalline lamellar structure. It has been found in rhombohedral crystals, isomorphous with those of arsenic. By melting antimony in a crucible, allowing it to cool slowly until the surface has solidified, and then pouring out the still liquid portion from the interior, it may also be obtained artificially as a mass of well defined rhombohedrons. The strong tendency of antimony to crystallize is well shown in the commercial cakes of the metal, which usually present upon their upper surfaces beautiful stellate, or fern-like markings. The sp. gr. of antimony is from 6·60 to 6·85. It is an inferior conductor of heat and electricity. At 450° it melts, and at white heat may be distilled, though with difficulty, in an atmosphere of hydrogen. It gives off vapours, however, when merely raised to a full red heat. It is not

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sensibly altered by exposure to dry or moist air, at ordinary temperatures, but oxidates quickly when heated to its melting point. Heated to full redness in the air, it takes fire, and, if tolerably pure, burns brilliantly, with copious evolution of inodorous white vapours of the teroxide. Powdered antimony takes fire when thrown into chlorine gas, and combines very energetically with bromine and iodine. It is oxidated readily by nitric acid, with formation of an insoluble oxide of antimony, either the pentoxide, or some mixed oxide, according to the strength of the acid employed. It is unaffected by dilute sulphuric acid, and scarcely indeed by the strong acid, unless heated therewith, when it is converted into sulphate of antimony, with evolution of sulphurous anhydride. In the massive state, it is not acted upon by aqueous chlorhydric acid; but when finely powdered, it is dissolved by the boiling acid, with evolution of hydrogen. It dissolves readily in chlorhydric acid to which a little nitric acid has been added, forming a solution of trichloride of antimony, in which water will produce a white precipitate, provided the excess of acid has first been driven off. Powdered antimony is also dissolved readily by solutions of alkaline polysulphides, with formation of sulphantimonites and sulphantimonates.

When weak antimonial solutions are electrolysed, the metal is deposited upon the negative pole in the crystalline state. It has usually a silver-grey colour, a frosted surface, a hard texture, a radiated crystalline structure, and a sp. gr. of about 6·6. But Gore has shown that under certain circumstances there is deposited from strong solutions of antimony a peculiar amorphous metal, which has a dark steel colour, a smooth mamillated surface, a comparatively soft texture, a lustrous amorphous fracture, and a sp. gr. varying from 5·74 to 5·83. Gore finds that this amorphous antimony is very readily deposited from a solution of one part of tartar emetic in four parts of commercial chloride of antimony; but many other solutions may be used. The electrolysis can be effected with two or three of Smee's cells, but the intensity of the current may be varied within very wide limits. Gore's amorphous antimony always contains five or six per cent. of chloride of antimony and a trace of chlorhydric acid, whether or not retained mechanically within the mass is not evident. When gently heated or sharply struck, amorphous antimony undergoes a peculiar molecular change, attended with great manifestation of heat, the temperature rising from 15° to 230° and upwards, and with an evolution of fumes of chloride of antimony. The metal so changed approximates to the crystalline variety in its structure, density, and colour. By care-

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fully triturating thin pieces of amorphous antimony in ice-cold water, it may be obtained as a fine powder, which, when afterwards heated or struck, will exhibit its characteristic molecular transition. The specific heat of unchanged amorphous antimony was found by Gore to be 0·0631, and after its sudden discharge of heat, only 0·0543.

Stibamine.

Symbol, H_3Sb; *Proportional number*, 123.

(372) This gas, also known as antimonetted hydrogen, has not been obtained pure, but always mixed with a variable proportion of free hydrogen. It is best made by dissolving an alloy of antimony with a large excess of zinc in aqueous chlorhydric, or in dilute sulphuric acid:—

$$Zn_3Sb + 3HCl = H_3Sb + 3ZnCl.$$

Most antimonial solutions in contact with nascent hydrogen, particularly when developed from zinc and dilute acid, become decomposed, some portion of the antimony being reduced to the metallic state, and another portion being hydrogenetted into stibamine.

Antimonetted hydrogen is a colourless gas, inodorous if free from arsenamine, and quite insoluble in water. It is decomposed below a red heat into metal and hydrogen. It burns in the air with a bluish-white flame, and gives off an opaque white smoke of teroxide of antimony. When the free combustion of the gas is interfered with, by depressing a cold porcelain surface on the flame, for instance, the hydrogen only is burnt, while metallic antimony is thrown down as a smoke-black deposit on the porcelain. Stibamine passed into solution of nitrate of silver, causes a precipitate of antimonide of silver, whereas arsenamine throws down metallic silver only (vide par. 345):—

$$3AgNO_3 + H_3Sb = 3HNO_3 + Ag_3Sb.$$

From the composition of the antimonide of silver so produced, that of antimonetted hydrogen has been inferred. The gas, when passed into strong nitric acid, yields a white deposit of pentoxide of antimony.

Stibamine may be looked upon as a general type from which many antimonial compounds are derived. Thus we have metal-derivatives, the antimonides of silver and zinc, for instance, Ag_3Sb and Zn_3Sb respectively; halogen-derivatives, the chloride and bromide, for instance, Cl_3Sb and Br_3Sb respectively; and alcohol-

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radicle derivatives, stibethyl and stibamyl, for instance, Et_3Sb and Am_3Sb respectively, &c.

(373) The properties of antimonetted hydrogen, and the circumstances of its formation, enable us to employ Marsh's process for the detection of antimony as well as for that of arsenic. It sometimes happens, however, under unascertained conditions, that the whole of the antimony present in a compound is deposited in the metallic state upon the zinc, without a trace of stibamine being formed. The antimonial stain produced by depressing a piece of glass or porcelain upon the flame of hydrogen containing antimonetted hydrogen, is characterized: α, by its comparative want of metallic lustre; β, by its smoky-black colour; γ, by its non-volatility, save at a red heat; δ, by its insolubility in chloride of lime; ε, by its ready solubility in yellow sulphide of ammonium, so as to form a solution which, on evaporation to dryness, leaves a bright orange stain; ς. and by its yielding, after treatment with nitro-muriatic acid and evaporation to dryness, a residue which does not give a red precipitate with nitrate of silver solution (vide par 347). If it be only warmed with nitric acid, a residue containing teroxide of antimony is left, which produces a black deposit with ammonio-nitrate of silver.

The antimonial deposit, produced by heating a current of antimonetted hydrogen during its transmission through a glass tube, is characterized by its position at the exact spot where the heat is applied, by its want of volatility, and by its non-convertibility into arsenious anhydride or arsenic acid. The piece of tube containing the deposit may be cut off and boiled in a weak and slightly alkaline solution of permanganate of potassium, whereby a solution of antimonate of potassium will be formed. This may be filtered off, and after acidulation with chlorhydric acid, be tested with sulphuretted hydrogen, which will produce in it an orange precipitate of sulphide of antimony, capable of being further examined. In testing for antimony by the production of stibamine, an electrolytic cell may be substituted for the Marsh's apparatus, but even with several of Grove's cells a part only of the antimony becomes hydrogenetted, the remainder being deposited in the metallic state upon the negative pole. Bloxam has shown that when a mixture containing both antimony and arsenic is oxidized with chlorhydric acid and chlorate of potassium, evaporated down, and introduced into the decomposing cell, the antimonic acid is alone reduced, with production of stibamine, while the arsenic acid remains unaffected. But on adding sulphuretted hydrogen to the liquid, the

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formation of stibamine is arrested, through conversion of the antimony into the state of an insoluble sulphide, while the excess of sulphuretted hydrogen gradually reduces the arsenic acid to the state of arsenious acid, which the current simultaneously deoxidates into arsenetted hydrogen. Moreover, if a mixture containing arsenic and antimonic acids be treated with sulphuretted hydrogen in excess, and the filtered liquid be poured into a Marsh's apparatus, the evolved gas will contain arsenetted, but will be free from antimonetted hydrogen.

ANTIMONIDES.

(374) Antimony combines with most other metals, including those of the alkalies, to form metallic alloys. A few antimonides occur native; some result from definite chemical reactions; while the majority are made by fusing antimony with the metals to be alloyed. The antimonides of definite composition are principally trimetallic and dimetallic. The trimetallic compounds may be looked upon as metal derivatives of arsenamine. We have an antimonide of zinc Zn_3Sb, made by fusing together the requisite proportions of zinc and antimony. It crystallises in long acicular prisms belonging to the right prismatic system, and decomposes boiling water rapidly, with evolution of hydrogen (Cooke). Antimonide of silver Ag_3Sb, is formed by decomposing a silver salt with antimonetted hydrogen, as we have seen, and corresponding antimonides of copper, mercury, &c., may be formed by the same process. A native antimonide of silver, known as dicrasite, has the formula Ag_6Sb, or probably $(Ag_2)_3Sb$. Among dimetallic compounds, we have native antimonide of nickel or breithauptite Ni_2Sb, which occurs crystallized in thin hexagonal plates, and has also been formed artificially. Another antimonide of zinc Zn_2Sb, has been prepared by fusing the two metals together. It crystallizes in broad rhombic plates, and decomposes boiling water, though less readily than the trizincide. One form of dicrasite also has the formula Ag_4Sb, or rather $(Ag_2)_2Sb$.

The introduction of antimony adds to the hardness and brittleness of nearly all heavy metals with which it is alloyed. Type-metal is an alloy of lead and antimony, usually containing about 20 per cent. of antimony. Small proportions of tin and bismuth are sometimes added. This alloy expands considerably in the act of solidification, and is not unduly soft on the one hand or brittle on the other. Alloys of antimony with tin, or tin and lead, and occasionally small quantities of other metals, are much used for

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machinery bearings. Britannia-metal is the name applied to various alloys. Some consist of tin, with about ten per cent. of antimony, others of antimony, tin, brass, lead, and bismuth, in about equal proportions.

Halogen compounds of Antimony.

(375) Trichloride of Antimony. *Sym.* Cl_3Sb; *p.n.* 226·5; *v.d.* 113·25; □□.—Antimony unites directly with chlorine gas to form either a trichloride or pentachloride of the metal. *α.* The trichloride may be made by passing chlorine slowly through a tube containing an excess of powdered antimony, or of heated trisulphide of antimony. In the latter case, the product must be gently heated for some time to volatilize the chloride of sulphur formed simultaneously. *β.* Trisulphide of antimony may be dissolved in heated chlorhydric acid, or metallic antimony in the same acid to which a little nitric acid is occasionally added, and the resulting liquid, after evaporation to an oily consistency, distilled. *γ.* Metallic antimony or the trisulphide may be heated with corrosive sublimate, when the trichloride is produced, as shown in the following equations: —

$$Sb_2 + 4HgCl = Cl_3Sb + Hg_2Sb + Hg_2Cl.$$
$$Sb_2S_3 + 6HgCl = 2Cl_3Sb + 3Hg_2S.$$

δ. It is sometimes made by distilling sulphate of antimony with common salt: $Sb_2(SO_4)_3 + 6NaCl = 3Na_2SO_4 + 2Cl_3Sb$.

At ordinary temperatures, trichloride of antimony is a translucent yellowish substance having a fatty consistency, whence its popular name, butter of antimony. It melts at 72°, and boils at 223°. It fumes slightly in the air, and volatilizes to an appreciable extent in boiling aqueous chlorhydric acid. It is deliquescent and highly corrosive. It dissolves unchanged in aqueous chlorhydric acid, and in a small quantity of water, but is decomposed by a large quantity of water, with formation of chlorhydric acid and a white precipitate of oxichloride of antimony SbClO, or chloride of antimonyl (SbO)Cl (Peligot): $SbCl_3 + H_2O = SbClO + 2HCl$. This oxichloride is readily fusible, and on cooling solidifies as a translucent crystalline mass. By the continued action of water, especially of hot water, it is gradually decomposed, with conversion into a more basic compound, formerly known as powder of algaroth. Trichloride of antimony unites directly with ammonia to form the compound $NH_3.SbCl_3$, and produces crystalline double salts with the chlorides of ammonium and the alkali-metals.

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(376) PENTACHLORIDE OF ANTIMONY. *Sym.* Cl_5Sb; *p. n.* 297·5. —This compound is formed, with brilliant combustion, when powdered antimony is thrown into chlorine gas. It is usually made by acting upon coarsely-powdered antimony with dry chlorine, or by passing the gas into melted trichloride of antimony. It occurs as a yellowish fuming liquid, which solidifies at zero into a crystalline mass. When distilled, it undergoes a partial decomposition into the trichloride and free chlorine, whence it constitutes a very useful chlorinetting agent. Olefiant gas C_2H_4, for instance, is converted by its passage through boiling pentachloride of antimony, into Dutch liquid $C_2H_4Cl_2$. With a small quantity of water, it forms white deliquescent crystals, probably of an oxichloride of antimony Cl_3SbO, analogous to oxichloride of phosphorus Cl_3PO. By a large quantity of water, it is converted into antimonic and chlorhydric acids. It absorbs sulphuretted hydrogen at ordinary temperatures, forming a white crystalline mass of sulphochloride of antimony Cl_3SbS.

(377) TRIBROMIDE OF ANTIMONY. *Sym.* Br_3Sb; *p. n.* 200.— Finely powdered antimony takes fire when thrown into bromine vapour, with production of this compound. It is usually made by adding antimony, little by little, to liquid bromine contained in a retort, and agitating after each addition. The product is purified by distillation. Tribromide of antimony occurs as a white deliquescent mass of crystalline needles. It melts at 90°, and boils at 270°. Water decomposes it, forming an oxibromide SbBrO. *Teriodide of antimony* I_3Sb, is prepared by triturating antimony with iodine. It is a deliquescent crystalline solid, of a brown-red colour. It is fusible and volatile without decomposition. Water reacts with it to produce an oxiodide SbIO. A fluor-compound of antimony said to be the *trifluoride* F_3Sb, is made by dissolving the teroxide in fluorhydric acid. It forms colourless crystals, which are soluble in water, without decomposition.

OXYGEN COMPOUNDS OF ANTIMONY.

(378) TEROXIDE OF ANTIMONY. *Sym.* Sb_2O_3; *p. n.* 288.—*α.* Antimonious oxide constitutes a somewhat rare mineral, known as valentinite, which occurs crystallized in shining white prisms belonging to the right prismatic system. Their sp. gr. is 5·56, and hardness from 2·5 to 3·0. It has also been found crystallized in regular octahedrons, and is known in this form as senarmontite. *β.* Teroxide of antimony results from the combustion of the metal in air. When antimony is heated to full redness in an imperfectly

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covered crucible, antimonious oxide is produced, and is usually deposited upon the sides of the crucible in the form of prismatic crystals. Sometimes, however, when the metal is heated till it begins to burn, and then left to cool slowly, regular octahedrons are formed intermixed with the prisms. γ. A ready mode of obtaining antimonious oxide consists in pouring a chlorhydric acid solution of trichloride of antimony, prepared by dissolving trisulphide of antimony in chlorhydric acid and diluting slightly with water, into a boiling solution of carbonate of sodium, when the compound is precipitated as a crystalline powder. Or trisulphate of antimony may be decomposed in a similar manner by means of carbonate of sodium.

Teroxide of antimony is a white or greyish white crystalline solid. It is isodimorphous with arsenious anhydride, the ordinary form of the one compound corresponding to the rare form of the other. On the application of heat, it becomes temporarily yellow, at a red heat it melts, and at a higher temperature may be volatilized in close vessels, so as to produce a sublimate of prismatic crystals. Heated to redness in the air, it becomes transformed into the tetroxide with a tinder-like combustion. It is readily reduced to the metallic state by ignition with hydrogen, charcoal, black flux, &c. Teroxide of antimony is very slightly soluble in water, but freely so in aqueous chlorhydric acid, forming a transparent solution provided no antimonic oxide is present. It also dissolves in a hot solution of tartaric acid, and still more easily in one of acid tartrate of potassium or cream of tartar. It is insoluble in ordinary nitric acid, but dissolves in fuming sulphuric acid, and is deposited therefrom in shining anhydrous scales of trisulphate of antimony.

(379) ANTIMONIOUS HYDRATE. *Sym.* $HSbO_2$; *p.n.* 153.—The normal, or trihydrate H_3SbO_3, is unknown. The meta- or monhydrate results from pouring a solution of trichloride of antimony into one of carbonate of sodium, either cold or only slightly warm. At a boiling heat it loses water to become the teroxide:— $2HSbO_2 - H_2O = Sb_2O_3$. It dissolves readily in solutions of potash and soda, forming very unstable antimonites, which are decomposed by ebullition or evaporation, with separation of prismatic crystals of the teroxide. According to Mitscherlich, its solution in boiling soda deposits the teroxide in octahedral crystals.

(380) The functions of antimonious oxide and hydrate are rather basylous than acidulous. In the antimonites, indeed, the antimony constitutes the chlorous radicle; but these compounds

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are very unstable and ill-defined. Antimonial salts are of two kinds; those in which three atoms of hydrogen are displaced by one atom of antimony Sb‴, and those in which one atom of hydrogen is displaced by one atom of antimonyl (SbO)′, as shown in the chlorides and double tartrates, &c.*

Chlorhydric acid . .	HCl	$(SbO)'Cl$	Chloride of antimonyl.
Ditto three atoms . .	H_3Cl_3	$Sb'''Cl_3$	Trichloride of antimony.
Acid tartrate of potassium	$C_4H_5KO_6$	$C_4H_4(SbO)'KO_6$	Tartar emetic (basic).
Ditto plus tartaric acid	$C_8H_{11}KO_{12}$	$C_8H_8Sb''KO_{12}$	Neutral tartar emetic.
Acid oxalate of potassium	C_2HKO_4	$C_2(SbO)'KO_4$	Potas-oxalate antimony.
Three atoms sulphuric acid	$H_6S_3O_{12}$	$Sb_2^{'''}S_3O_{12}$	Trisulphate antimony.

Antimony salts are for the most part colourless compounds. Heated on charcoal before the blow-pipe, they furnish an abundant white incrustation, and a bead of brittle metal. The normal salts of antimony, in which Sb‴ displaces H_3, are either insoluble in water, or decomposed thereby, with formation of insoluble basic compounds. Acidulated solutions of antimony salts, unless too strongly acid, are also decomposed by water, with production of white precipitates. These precipitates do not form in the presence of tartaric, citric, and some other vegetable acids, which also dissolve the precipitates when already thrown down. The precipitates produced by water in antimony solutions are distinguished from the similar precipitates produced in bismuth solutions by their solubility in tartaric acid, and by their becoming orange-coloured when treated with sulphuretted hydrogen (vide par. 396). This gas produces in all acidulated antimonial solutions an orange-red precipitate of sulphide of antimony, which is insoluble in cold dilute chlorhydric acid, and in solutions of carbonate of ammonium and acid sulphite of potassium, but is soluble at a gentle heat in strong chlorhydric acid, in aqueous hydrates, sulphydrates, and sulphides, and at a boiling heat in solutions of fixed alkaline carbonates. The basylous metals, zinc, cadmium, iron, copper, and tin, displace antimony from its acidulated solutions, the first two more especially, with evolution of antimonetted hydrogen (vide par. 373). A piece

* It is a general, and indeed almost an obvious law, that the equivalency of any simple or compound radicle is decreased by its association with some other radicle of an opposite electro-chemical function, in the exact proportion of the equivalent values of the two. Thus Sb‴ is terequivalent; but Sb‴ combined with O″, is monequivalent, because two-thirds of its basylous equivalency are neutralised by the diequivalent oxygen.

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of tin immersed in a cold acidulated antimonial solution becomes quickly covered with a black pulverulent coating of metallic antimony. When metallic copper is boiled in even a very dilute solution of antimony acidulated with chlorhydric acid, it soon acquires a lustrous purple coating of antimonide of copper. The coated copper, when dried and heated in a reduction-tube, either yields no sublimate at all, or else a slight fixed, amorphous, white deposit, by which behaviour it is distinguished from copper coated with arsenic. When boiled with a weak alkaline solution of permanganate of potassium, the antimony is dissolved away from the copper in the form of antimonate of potassium; or if the antimonial coating be not very thick, it will suffice to boil the copper for some time, with frequent exposure of its surface to the air, in a weak solution of caustic potash only. (Watson.) Either of these solutions may be acidified and treated with sulphuretted hydrogen, when an orange-coloured precipitate of sulphide of antimony will be obtained, which may be dissolved in chlorhydric acid, and the resulting solution tested for antimony by all the usual processes. The above is a very convenient method of extracting antimony from organic mixtures, as in cases of suspected poisoning, &c. The acidulated solution of an antimony salt slowly reduces trichloride of gold, with precipitation of metallic gold. In alkaline solutions of antimony, that is, in antimonites, chloride of gold and nitrate of silver each produce immediate black precipitates, which are insoluble in ammonia.

(381) TETROXIDE OF ANTIMONY. *Sym.* Sb_2O_4; *p. n.* 304.—*α.* This oxide is found native as cervantite, either in the massive state or in acicular crystals. It has a yellowish-white colour, a greasy lustre, and a sp. gr. of 4·08? *β.* It is made artificially by igniting the pentoxide Sb_2O_5, or by roasting the teroxide Sb_2O_3, or by acting upon powdered antimony with excess of nitric acid, and heating the residue. It occurs as a yellowish-white powder, of sp. gr. 6·69, which becomes temporarily yellow when hot. It is infusible and unalterable in composition by heat. It is easily resolved into antimonious and antimonic oxides, or their corresponding compounds:— $2Sb_2O_4 = Sb_2O_3 + Sb_2O_5$. Thus it dissolves to some extent in aqueous chlorhydric acid to form a solution, which when mixed with a large quantity of water, is decomposed, with precipitation of antimonious oxide or oxichloride, while antimonic hydrate remains in solution. Again; when boiled with a solution of cream of tartar, it is resolved into antimonious oxide, which dissolves, and antimonic acid, which is left unacted upon. When the tetroxide is

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fused with hydrate or carbonate of potassium, and the resulting mass washed with cold water, there is left an antimonoso-antimonate of potassium $K_2Sb_2O_5$, or $KSbO_2.KSbO_3$, which may be dissolved in boiling water, and re-obtained, on evaporation, as a yellow amorphous saline mass. A few similar bodies have been found native; romeine, or antimonoso-antimonate of calcium, for instance, $Ca_2Sb_2O_5$? Fremy doubts the existence of this class of compounds; but it must be remembered that similar nitrogen bodies have been obtained, cobalt yellow, for instance, $Co_2N_2O_5$. Tetroxide of antimony is sparingly soluble in water, forming an acid solution. The solid hydrate $H_2Sb_2O_5$, or $H_2O.Sb_2O_4$, may be obtained as a white precipitate by decomposing the solution of antimonoso-antimonate of potassium with an acid. The same compound apparently has been obtained in nacreous acicular crystals by carefully evaporating a solution of the tetroxide in aqueous chlorhydric acid.

(382) PENTOXIDE OF ANTIMONY. *Sym.* Sb_2O_5; *p. n.* 320.—Antimonic oxide or anhydride may be made by gently heating the corresponding hydrate or acid. It is a yellowish-white powder, of sp. gr. 6·6, which is insoluble in water and acids. At a red heat it gives off oxygen, with conversion into the tetroxide. When fused with carbonate of potassium, it forms an antimonate, with expulsion of carbonic anhydride.

(383) ANTIMONIC ACIDS OR HYDRATES.—Much confusion exists in reference to these compounds, owing to the facility with which they pass into one another. There appear to be three distinct hydrates:—

Orthantimonic acid	H_3SbO_4
Antimonic acid	$HSbO_3$, or $H_3SbO_4 - H_2O$
Parantimonic acid	$H_4Sb_2O_7$, or $H_3SbO_4 + HSbO_3$.

When pentachloride of antimony is acted upon by water, a white precipitate is produced, which the strongest analogy warrants us in believing to be orthantimonic acid. An oxichloride of antimony is first formed, which the further action of water decomposes, with the customary exchange, atom to atom, of peroxide of hydrogen HO, for chlorine Cl:—

$$Cl_5Sb + H_2O = Cl_3SbO + 2HCl.$$
$$Cl_3SbO + 3H_2O = H_3SbO_4 + 3HCl.$$

The precipitate is soluble in ammonia at ordinary temperatures, and in a large quantity of distilled water; but is thrown down from

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its aqueous solution on the addition of an acid. It is very unstable, and soon changes into common antimonic acid, even when kept under water.

Common antimonic acid $HSbO_3$, corresponds in its formula to nitric acid HNO_3, and is the most stable of all the antimonic hydrates. By analogy it should be called metantimonic acid, but this name having been applied by Fremy to another compound, it may be termed, by way of distinction, monantimonic acid. It results from the dehydration, spontaneous or otherwise, of the ortho- and para- acids, and from the treatment of metallic antimony with strong nitric acid, to which it is advantageous to add a little chlorhydric acid. Its composition, as determined by Berzelius, is perfectly definite. According to Fremy, it also occurs in the state of a bihydrate $HSbO_3 . 2H_2O$. It is a soft yellowish-white powder, practically insoluble in water, though imparting to it an acid reaction. It is insoluble also in cold ammonia, but soluble in caustic potash, and to some extent in strong chlorhydric acid. Its solution in chlorhydric acid gradually yields a precipitate of some form of antimonic acid, when diluted with a small quantity of water, but remains permanently clear when a large quantity of water is added.

Parantimonic acid $H_4Sb_2O_7$, is the analogue of pyrophosphoric acid $H_4P_2O_7$, and constitutes the metantimonic acid of Fremy. It is formed by acidifying the solution of an alkaline parantimonate. Its properties resemble those of the ortho- acid. It speedily undergoes a spontaneous conversion into monantimonic acid $HSbO_3$.

(384) ANTIMONATES.—A hydrated trimetallic antimonate of lead $Pb_3SbO_4 . 2H_2O$ has been found native. The pigment known as Naples yellow, made by igniting a mixture of one part of tartar-emetic and two parts of nitrate of lead with four parts of common salt, and then washing out the fused common salt, is an anhydrous antimonate of lead, probably a tris-antimonate. Monantimonate of potassium $KSbO_3$, is obtained by fusing antimonic oxide with carbonate of potassium, to which a little nitre may be advantageously added, especially when any tetroxide is present. Or metallic antimony may be deflagrated with nitre. The mass resulting from either operation, having been washed with cold water, is to be boiled in more water for some time, when it will gradually dissolve. The solution so formed produces with salts of the heavy metals hydrated precipitates, which lose water on drying, and become monantimonates $MSbO_3$. The nature of the

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solution itself is very doubtful. It not improbably contains the orthosalt KH_2SbO_4. When evaporated down it leaves a gummy residue, the composition of which, as determined by Fremy, is expressed by the formula $2KSbO_3.5H_2O$, or possibly $2(KH_2SbO_4.H_2O)$? The residue heated to 160° loses two atoms of water, and becomes insoluble.

When the above solution of monopotassic antimonite is evaporated to a syrupy consistency in a silver dish, and fragments of hydrate of potassium added from time to time, an unstable, parantimonate of potassium is gradually formed: $2KSbO_3 + 2KHO = K_4Sb_2O_7 + H_2O$. On evaporating the liquid still further, and allowing it to cool, a crystalline mass is obtained, which is to be separated from the strongly alkaline liquid and dried on a tile. After the crystals have been washed quickly with a little water to convert the neutral into the acid salt and remove the excess of potash, the residue may be dissolved in a fresh portion of water. The solution of acid parantimonate of potassium $K_2H_2Sb_2O_7$, so formed, gives with sodium salts a crystalline precipitate of acid parantimonate of sodium $Na_2H_2Sb_2O_7.6H_2O$. Acid parantimonate of potassium solution speedily becomes altered by keeping, so as no longer to give any precipitate with sodium-salts. It is termed acid metantimonate of potassium by Fremy.

The precipitate produced by sulphuretted hydrogen in acidified antimonic solutions is of a paler colour than that produced in antimonious solutions. A chlorhydric acid solution of antimonic acid or an antimonate decomposes iodide of potassium solution with liberation of iodine. Trichloride of gold gives no precipitate in alkaline solutions of antimonates, and that formed by nitrate of silver is soluble in ammonia. The liberation of iodine by antimonic compounds, and peculiar decomposition of gold and silver salts by antimonious compounds, serve to identify readily the presence of one, or other, or both sets of bodies.

Compounds of Antimony and Sulphur.

(385) **Oxisulphide of Antimony.** *Sym.* Sb_2S_2O; *p. n.* 320.—This compound may be looked upon as trisulphide of antimony Sb_2S_3, in which an atom of sulphur is replaced by one of oxygen. It constitutes a somewhat rare mineral, known as red antimony. It occurs in tufts of capillary crystals belonging to the oblique prismatic system. Its sp. gr. is from 4·5 to 4·6. It has a bright red colour and brilliant earthy lustre. It melts readily before the blow-pipe.

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Many oxisulphides of antimony have been prepared artificially, but they do not constitute definite chemical compounds. Crocus of antimony is the name applied to a substance obtained by fusing teroxide with trisulphide of antimony, and in several other ways, as well as to the scoriæ produced by antimony smelters. When trisulphide of antimony is heated in the air it gradually loses sulphur and acquires oxygen, with conversion into a grey powder, which, by an increase of heat, fuses into a transparent yellow-brown substance known as glass of antimony. It contains about 15 per cent. of sulphide and 85 per cent. of oxide of antimony. Some varieties of the body known as kermes, which will be presently described, are thought to be oxisulphides of antimony.

(386) TRISULPHIDE OF ANTIMONY. *Sym.* Sb_2S_3; *p. n.* 336.—Antimonious sulphide exists in the crystalline and amorphous conditions. The native crystallized sulphide, known as grey antimony ore or stibnite, the *stibium* of the ancients (*στίβι*), is the mineral from which all the antimony of commerce and the different preparations of the metal are obtained. It is found among beds of primitive rock in many parts of the world, in masses of acicular crystals belonging to the right prismatic system. The native sulphide, separated from its gangue by simple fusion, is known in commerce as crude antimony. It occurs in roundish lumps or cakes, which, when broken, present a striated highly crystalline appearance. It is usually contaminated with other sulphides, those of lead, iron, copper, and arsenic, for instance. *β.* Crystallized trisulphide of antimony may be made artificially by fusing any form of the amorphous sulphide, or by heating sulphur either with metallic antimony or antimonious oxide: $2Sb_2O_3 + S_9 = 2Sb_2S_3 + 3SO_2$.

Crystalline sulphide of antimony is an opaque brittle solid, of sp. gr. from 4·5 to 4·6, having a steel-grey colour, and strong metallic lustre. It fuses below a red heat, and volatilizes at a white heat. Heated in the air, it absorbs oxygen and evolves sulphur in the form of sulphurous anhydride. It is readily desulphurized at high temperatures by hydrogen, charcoal, metallic iron, &c. It dissolves in aqueous chlorhydric acid at a boiling heat, with formation of trichloride of antimony and sulphuretted hydrogen. It dissolves still more readily in nitro-muriatic acid, with separation of sulphur. Strong nitric acid converts it into oxide and sulphate of antimony. Boiled with sulphuric acid, it forms trisulphate of antimony and sulphurous anhydride. Deflagrated

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with excess of nitre, it produces sulphate and antimonate of potassium. Its behaviour with alkalies will be presently referred to.

Amorphous sulphide of antimony is procurable by several processes. *α.* The native trisulphide, fused at a high temperature, is suddenly cooled by immersion in a large quantity of cold water (Fuchs). The product is an amorphous mass, having a conchoidal fracture, a sp. gr. 4·15, and a hardness greater than that of the crystalline variety. Its colour in thin pieces is hyacinth-red, in the state of powder, orange-brown. *β.* An anhydrous amorphous trisulphide may be obtained as a red precipitate, by boiling a chlorhydric acid solution of trichloride of antimony with thiosulphate of sodium:—

$$3H_2O + 3Na_2SO_3S + 2SbCl_3 = (6HCl + 3Na_2SO_4) + Sb_2S_3.$$

γ. When sulphuretted hydrogen is passed into an acidulated solution of an antimony-salt, that of tartar emetic, for instance, a bright orange-red precipitate of a hydrated trisulphide of antimony is formed, which may be rendered anhydrous, at a moderate heat, without losing its red colour. *δ.* It may also be made by acidulating the solutions of alkaline sulphantimonites.

Amorphous sulphide of antimony resembles the crystalline body in its behaviour with reagents, save that it is more readily acted on. When melted and allowed to cool spontaneously, it assumes the crystalline form. The recently-precipitated sulphide dissolves in a large quantity of boiling water, with evolution of sulphuretted hydrogen.

(387) SULPHANTIMONITES.—Many of these compounds occur native. In several of them a portion of the antimony is usually replaced isomorphously by arsenic, as in the Fahl-ores, red silvers, and bournonites. We have the usual varieties, ortho-, meta-, and para-, as shown below:—

Orthosalts M_3SbS_3	Pb_3SbS_3	Boulangerite.
	Ag_3SbS_3	Dark red silver.
	$Pb_2CcuSbS_3$	Bournonite.
Metasalts $M_3SbS_3—M_2S$	$PbSbS_2$	Zinkenite.
	$AgSbS_2$	Myargyrite.
	$CcuSbS_2$	Antimony-copper glance.
	$FeSbS_2$	Berthierite.
Parasalts $M_3SbS_3+MSbS_2$	$Pb_4Sb_2S_5$	Feather ore.
	$(CcuFe)_4Sb_2S_5$	Fahl ore.

Polybasite is a superbasic orthosulphantimonite of silver and

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cuprosum $(AgCcu)_3SbS_3 . 3(AgCcu)_2S$. Aqueous sulphantimonites of the alkali-metals give with soluble salts of the heavy metals dark coloured precipitates, which have not been minutely examined, but which are believed to be trimetallic or orthosulphantimonites.

The formation of sulphantimonite solutions, their deposition of kermes, and decomposition by acids, have been subjected to repeated examination, but the results attained are not altogether conclusive. When precipitated trisulphide of antimony is agitated with excess of cold potash, there is produced a mixture of sulphantimonite of potassium, and teroxide of antimony dissolved in the excess of potash: —

$$2Sb_2S_3 + 6KHO = 2K_3SbS_3 + Sb_2O_3 + 3H_2O.$$

On pouring this solution into a dilute acid, the whole of the antimony is thrown down as trisulphide, without any evolution of sulphuretted hydrogen, because the exact proportion of gas evolved from the sulphantimonite is absorbed by the dissolved teroxide:—

$$6HCl + 2K_3SbS_3 = 6KCl + Sb_2S_3 + 3H_2S.$$
$$3H_2S + Sb_2O_3 = 3H_2O + Sb_2S_3.$$

But when excess of precipitated sulphide of antimony is treated with cold potash, the alkaline liquid is incapable of retaining in solution the whole of the antimonious oxide produced in the reaction, some portion of which consequently attaches itself to the undissolved sulphide, so as to form a crocus of antimony. Hence on acidifying the clear solution, some sulphuretted hydrogen is always evolved, because there is not sufficient teroxide present to absorb the whole.

When an excess of antimonious sulphide, crystalline or amorphous, is boiled in caustic alkali, the hot liquid takes up a much increased proportion of the sulphide, but on cooling deposits the additional quantity in the state of a brown-red precipitate, well known as kermes. This precipitate always retains a small quantity of sulphantimonite of alkali-metal, and not unfrequently carries down some teroxide of antimony, minute crystals of which have been recognised in it by microscopic examination. On acidifying the cold filtered liquid, a bright orange precipitate of antimonious sulphide, known as golden sulphur of antimony, is thrown down with evolution of sulphuretted hydrogen. Much the same precipitate is formed by acidifying the warm liquid before the deposition of its kermes. This last deposit is the oxisulphuret of antimony of the Pharmacopœia.

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Similar sulphantimonite solutions are obtained, with evolution of carbonic anhydride, by boiling trisulphide of antimony with alkaline carbonates; also by fusing the trisulphide with caustic or carbonated alkali, and boiling the residue with water.

During the exposure to air of hot sulphantimonite solutions, a process of oxidation takes place, whereby the sulphur set free from one portion of the salt converts another portion into the state of sulphantimonate, so that on acidulation some pentasulphide of antimony is precipitated along with the trisulphide. Sulphur is sometimes added to the hot sulphantimonite solution on purpose to produce a sulphantimonate.

When, instead of adding the sulphantimonite solution to the dilute acid, the acid is added to the sulphantimonite, a portion of the teroxide of antimony dissolved in the latter often escapes the action of the evolved sulphuretted hydrogen, so that the precipitate finally produced contains oxide as well as sulphide of antimony.

(388) PENTASULPHIDE OF ANTIMONY. *Sym.* Sb_2S_5; *p. n.* 400.— *a.* This compound, which is not found native, is made by passing sulphuretted hydrogen gas through pentachloride of antimony dissolved in aqueous tartaric acid. *β.* Or, by acidulating the solution of an alkaline sulphantimonate: —

$$6HCl + 2Na_3SbS_4 = 6NaCl + Sb_2S_5 + 3H_2S.$$

Pentasulphide of antimony is an orange-yellow amorphous powder. When heated in close vessels, it breaks up into sulphur and the trisulphide. Heated in the air it takes fire and burns with flame. It dissolves in boiling chlorhydric acid, with formation of trichloride of antimony, sulphuretted hydrogen, and sulphur. It also dissolves readily in alkaline sulphides, sulphydrates and hydrates, including aqueous ammonia.

(389) SULPHANTIMONATES. — Those of the alkali-metals are well defined hydrated crystalline salts, readily soluble in water. Their solutions react with salts of the heavy metals to produce dark coloured precipitates, which are trimetallic sulphantimonates. But that of cadmium Cd_3SbS_4, produced by adding the solution of a cadmium salt to one of sulphantimonate of sodium in excess, has an orange-yellow colour. The soluble sulphantimonates are made by fusing pentasulphide of antimony, or a mixture of the trisulphide and sulphur, with an alkaline sulphide; or by dissolving pentasulphide of antimony in the solution of an alkaline sulphydrate. Schlippe's salt, $Na_3SbS_4 . 9H_2O$, is produced by grinding trisulphide of antimony, sulphur, carbonate of sodium, and

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quicklime with water. The paste is digested with frequent agitation in a bottle full of hot water. After twenty-four hours or so, the clear liquid is filtered off and evaporated, when it deposits the salt in large transparent almost colourless tetrahedral crystals.

(390) SALTS OF ANTIMONY. — When antimony is acted upon by nitric acid, a small proportion of the metal enters into solution as a nitrate. Precipitated antimonious oxide dissolves in concentrated nitric acid, and on dilution a basic *nitrate of antimony* is thrown down, which by digestion in water is completely decomposed into nitric and antimonious acids. Metallic antimony when heated with sulphuric acid yields a white mass, which dissolves in excess of sulphuric acid and crystallizes therefrom in small needles of the *trisulphate* $Sb_2^{III}(SO_4)_3$. It is decomposed by water, with production of various basic salts. When precipitated antimonious oxide is boiled in solution of oxalic acid, a white crystalline powder is formed of *acid oxalate of antimonyl* $(SbO)'HC_2O_4$. It is insoluble in cold and decomposed by boiling water. Acid oxalate of potassium boiled with precipitated oxide of antimony forms a soluble *oxalate of antimony and potassium*, which separates in large prismatic crystals. Its formula is $Sb'''(KC_2O_4)_3.3H_2O$. Aqueous phosphoric acid dissolves a small quantity of antimonious oxide, forming a solution, from which small prismatic crystals of an *acid phosphate of antimony* or *antimonyl* have been obtained. When a chlorhydric acid solution of antimonious oxide is added to an aqueous solution of phosphate of sodium, a white precipitate of *phosphate of antimony*, probably $Sb'''PO_4$, is produced.

§ V. BISMUTH.

Symbol, Bi; *Proportional number*, 210.

(391) Bismuth was recognised as a distinct metal by Agricola, early in the 16th century. It is obtained principally from Saxony, Bohemia, and Transylvania. It occurs for the most part in the metallic state, dispersed through a matrix of quartz; but is also met with in the forms of oxide, carbonate, sulphide, double sulphide, and sulpho-telluride.

Bismuth is usually extracted from its matrix by fusion at a gentle heat. The ore is introduced into inclined iron tubes running across a furnace, and the melted metal is drawn off at the lowest extremity of each tube through a plugged opening. Com-

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mercial bismuth may be partly purified by fusing it with nitre, whereby the arsenic and sulphur which it usually contains are converted into arsenate and sulphate of alkali-metal. It is more completely purified by solution in nitric acid. The clear liquid is precipitated by a large excess of water, and the precipitated basic nitrate of bismuth reduced at a moderate heat with black flux. Native bismuth frequently contains silver, sometimes in sufficient proportion to render its extraction by cupellation remunerative.

(392) Bismuth is a tolerably hard, feebly sonorous metal. Though decidedly brittle, it may be slightly extended by careful hammering. Its aspect is lustrous, and its colour white, with a characteristic reddish-yellow tinge. Its sp. gr. is 9·8, which seems to be rather diminished than increased by strong pressure. It melts at 264° and solidifies with considerable expansion. It boils at a dull white heat, and if air be excluded condenses in laminæ. It vaporizes considerably at temperatures below its boiling point. Bismuth crystallizes after fusion in rhombohedrons, approximating very closely to cubes. It may be obtained in a very finely crystallized state by melting a few pounds in an iron ladle, allowing it to cool, piercing the crust formed on the surface, and pouring out the still fluid central portion of metal. A cup of bismuth lined with well-defined cuboid crystals, frequently having a beautiful iridescent appearance, is in this way procurable.

Bismuth is permanent in the air at ordinary temperatures, but is rapidly oxidized at a red heat. It combines readily with chlorine, bromine, iodine, and sulphur. The finely powdered metal even takes fire when thrown into chlorine gas or bromine vapour. Bismuth is scarcely affected by chlorhydric acid, but when heated with sulphuric acid, is rapidly acted upon, with formation of trisulphate of bismuth and evolution of sulphurous acid or anhydride. It dissolves readily in slightly diluted nitric acid, with formation of trisnitrate of bismuth and evolution of nitric oxide gas.

Bismuth promotes the fusibility of metals with which it is alloyed to a characteristic extent. The so-called *fusible metal* BiSnPb, is composed of one atom of bismuth (210 parts), one of tin (118 parts), and one of lead (104 parts). It fuses below 100°, previously undergoing a pasty condition. Solid fusible metal, like liquid water, undergoes an anomalous expansion by heat. It expands regularly from 0° to 35°, then contracts gradually to 55°, at which point it is less bulky than at 0°, again expands rapidly to 80°, and beyond that temperature continues expanding regularly up to its melting point.

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Halogen Compounds of Bismuth.

(393) Trichloride of Bismuth. *Sym.* $BiCl_3$; *p. n.* 316·5; *v. d.* 158·25; □□. — This compound is a representative of the unknown terhydride of bismuth H_3Bi. Other representatives are furnished by bismuth-ethyl Et_3Bi, bismuth-dichlorethyl $EtCl_2Bi$, &c. &c. *α.* Chloride of bismuth may be formed by passing dry chlorine gas over metallic bismuth, when combination takes place with very considerable energy. *β.* It may also be made by evaporating an acidulated aqueous solution of chloride of bismuth to dryness and distilling. *γ.* Or, by distilling a mixture of finely powdered metallic bismuth and chloride of mercury: —

$$6HgCl + Bi = 3Hg_2Cl + BiCl_3.$$

Trichloride of bismuth occurs as an opaque greyish white mass, having a granular fracture. It is readily fusible and volatile, deliquescent in moist air, and soluble in chlorhydric acid: similar solutions may be formed by dissolving the metal in nitro-muriatic, or its oxide in chlorhydric acid. When the solution of chloride of bismuth in chlorhydric acid is evaporated, a double chloride of bismuth and hydrogen, probably $BiCl_3 . 2HCl$, crystallizes out in fine needles. Similar double chlorides of bismuth with sodium and potassium are formed as hydrated crystalline salts, by evaporating acidulous solutions of the mixed chlorides. That of sodium has the formula $BiCl_3 . 2NaCl . 3H_2O$. It also crystallizes with only one atom of water.

Chloride of bismuth liquefies in a small quantity of water; but by a larger quantity, it is decomposed into oxichloride of bismuth BiClO, which precipitates, and aqueous chlorhydric acid holding a small quantity of chloride of bismuth in solution. Oxichloride of bismuth also results from precipitating with excess of water a not too acid solution of chloride of bismuth; from precipitating with chloride of potassium a not too acid solution of nitrate of bismuth; and from volatilizing chloride of bismuth in the presence of air. It is a white insoluble compound, becoming temporarily yellow when heated, and fusing at a red heat without decomposition. It is unaffected by dilute potash, and is deposited unchanged on the evaporation of its nitric acid solution.

(394) Tribromide of Bismuth. *Sym.* $BiBr_3$; *p. n.* 450. — This salt is made by dissolving bismuth in excess of bromine contained in a long test tube. On evaporating off the excess of halogen, it remains as a steel-grey compound, which melts at 200°, and boils at a red heat. It is converted by treatment with water into the

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oxibromide BiBrO. *Teriodide of bismuth*, BiI_3, is made by precipitating with iodide of potassium a solution of chloride or nitrate of bismuth in dilute acetic acid. It occurs as a brown crystalline precipitate, partially decomposed by washing, completely decomposed by boiling with water into the oxiodide BiIO. A *trifluoride of bismuth*, BiF_3, has been obtained by evaporating down a solution of bismuthous oxide in aqueous fluorhydric acid.

Oxygen Compounds of Bismuth.

(395) Teroxide of Bismuth. *Sym.* Bi_2O_3; *p.n.* 468.—This oxide constitutes the rare mineral known as bismuth-ochre. *a.* It may be readily obtained by heating bismuth in the air and stirring it constantly. When the metal is strongly heated in air or oxygen, it takes fire, and produces an abundant yellow smoke of bismuthous oxide. *β.* It may also be made by heating the nitrate, carbonate or hydrate of bismuth to dull redness; or by boiling the hydrate for some time in strong potash- or soda-ley.

Teroxide of bismuth is a pale yellow solid, of sp. gr. 8·2. On the application of heat, it becomes darker in colour, and soon melts into a brown liquid, which solidifies as a yellow crystalline mass. The oxide obtained from the hydrate by means of caustic alkali is also crystalline, forming yellow shining needles. Bismuthous oxide is easily reduced to the metallic state by ignition with hydrogen, charcoal, and many of the metals. It dissolves readily in chlorhydric, nitric, and other acids, with formation of bismuthous salts.

(396) Hydrate of Bismuth. *Sym.* $HBiO_2$; *p.n.* 243.—When nitrate of bismuth, dissolved in dilute nitric acid, is added to a weak solution of ammonia or caustic alkali in excess, a white flocculent precipitate, probably the trihydrate H_3BiO_3, is produced. On drying, it becomes more compact, and then constitutes the monhydrate $HBiO_2$, a perfectly definite compound, occurring as an opaque white amorphous powder. Teroxide of bismuth fused with an alkaline carbonate expels one atom of carbonic anhydride for each atom of bismuthous oxide, so as to form an unstable bismuthite of alkali-metal, corresponding to the monhydrate:—

$$Na_2CO_3 + Bi_2O_3 = 2NaBiO_2 + CO_2.$$

When precipitated hydrate of bismuth is boiled in a tolerably concentrated solution of fixed caustic alkali, it loses water, and is converted into the crystalline oxide:—

$$2HBiO_2 = Bi_2O_3 + H_2O.$$

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(397) Teroxide of bismuth reacts with the aqueous acids to form bismuthous salts. In the normal salts, one atom of bismuth displaces three atoms of hydrogen, thus:—

$$Bi_2O_3 + 6HCl = 3H_2O + 2Bi'''Cl_3$$
$$Bi_2O_3 + 6HNO_3 = 3H_2O + 2Bi'''(NO_3)_3.$$

Chemists are also acquainted with basic salts of bismuth, some of which are considered to contain the radicle bismuthyl, the crystalline suboxalate of bismuth $C_2H(BiO)'O_4$, for instance.

Bismuth salts are very heavy and, for the most part, colourless compounds. Heated on charcoal before the blowpipe, they yield a yellow incrustation and a brittle metal. The normal salts of bismuth are either insoluble in water or decomposed thereby, with formation of basic compounds. Acidulated solutions of bismuthous salts also, provided they are not too acid, are decomposed by excess of water, with the production of white precipitates, which are insoluble in tartaric acid, and turned black by sulphuretted hydrogen. All bismuthous solutions are decomposed by sulphuretted hydrogen gas, with precipitation of black trisulphide of bismuth, which is insoluble in dilute chlorhydric acid and in sulphide of ammonium. Caustic and carbonated alkalies produce in bismuthous solutions white precipitates which are insoluble in excess of the precipitants. The insoluble carbonates of the alkaline earth-metals also effect a complete decomposition of bismuthous solutions. The more basylous metals, zinc, cadmium, iron, copper, tin, &c., displace bismuth from its salts. Metallic copper boiled in even a very dilute bismuth solution acidified with chlorhydric acid, acquires a steel-grey coating of bismuth, or of an alloy of bismuth with copper. The binary or halogen salts of bismuth have been already considered. The principal ternary oxacid salts will be presently described.

(398) PENTOXIDE OF BISMUTH. *Sym.* Bi_2O_5; *p. n.* 500.—Bismuthic anhydride is a brown powder made by heating the acid or hydrate to a temperature of 130°:—

$$2HBiO_3 = Bi_2O_5 + H_2O.$$

When heated in a mercury bath it gives off oxygen, with conversion into bismuthous oxide; and is reduced to the same state by hydrogen gas, even at a lower temperature. Aqueous sulphurous acid converts bismuthic anhydride into sulphate of bismuth. Treated with chlorhydric acid it evolves chlorine, and with sulphuric acid, oxygen gas. It is unaffected by dilute nitric acid, but heated

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with the strong acid, it yields nitrate of bismuth and oxygen. According to Arppe, boiling nitric acid transforms it into a peculiar insoluble green oxide of bismuth Bi_4O_9. It is not acted upon by aqueous alkalies.

(399) BISMUTHIC ACID. *Sym.* $HBiO_3$; *p. n.* 259.—When precipitated bismuthous hydrate is boiled in a strong solution of caustic potash through which a brisk current of chlorine is being passed, it soon acquires a fine red colour, as does also the supernatant liquid. The red deposit, after being washed with water, is digested in dilute nitric acid, to remove the potash and bismuthous oxide, then again washed, and dried at 100°. A substance closely resembling the crude red product is made by adding bismuthous oxide to caustic potash kept fused for some time with free access of air. It also leaves bismuthic acid when treated with dilute nitric acid.

Bismuthic acid is moderately soluble in hot potash, and on gradually neutralising the solution, a reddish precipitate of bismuthate of potassium is thrown down, said to have the composition $KHO.Bi_2O_5$.

(400) Other oxides of bismuth have been described. Thus, when caustic potash is added to the solution of a bismuthous salt containing free chlorine, a yellow hydrated precipitate is produced which cannot be rendered free from chlorine by washing. When boiled with an alkaline hypochlorite containing excess of alkali, it becomes brown, and is then said to be a true *tetroxide* Bi_2O_4. It is perfectly soluble in hot nitric acid, a reaction which, according to Arppe, distinguishes it from the pentoxide. A *suboxide* of bismuth is also recognised by some chemists as a definite compound. It constitutes the film that forms on the surface of bismuth when heated to scarcely above its melting point. It is a brownish or purple-brown powder, which by treatment with aqueous chlorhydric acid, is resolved into bismuthous oxide, which dissolves, and metallic bismuth, which remains.

COMPOUNDS OF BISMUTH AND SULPHUR.

(401) DISULPHIDE OF BISMUTH. *Sym.* Bi_2S_2; *p. n.* 484.—This sulphide may be obtained as a radiated crystalline mass, frequently presenting clusters of distinct crystals in its interior, by quickly cooling a fused mixture of bismuth and sulphur. When bismuth and trisulphide of bismuth are fused together, the disulphide is also formed, and on cooling crystallizes out from the excess of melted metal. It occurs in acicular square prisms belonging to

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the right prismatic system. Its sp. gr. is 7·3. It has a greyish-white colour and high metallic lustre. In close vessels, it may be very strongly heated without evolving sulphur.

(402) TRISULPHIDE OF BISMUTH. *Sym.* Bi_2S_3; *p. n.* 516.—*α.* This sulphide is found native, as bismuth glance, a somewhat rare mineral, occurring both in the massive and crystalline states. Its sp. gr. is 6·4, its lustre metallic, and its colour bluish-grey. Its crystals are rhombic prisms belonging to the right prismatic system. *β.* It may be obtained by fusing together the requisite proportions of bismuth and sulphur, but sometimes the disulphide crystallises out even when an excess of sulphur is used. *γ.* Trisulphide of bismuth, probably in the hydrated state, is produced as a brownish-black amorphous precipitate, by decomposing the acidified solution of a bismuth salt with sulphuretted hydrogen:—

$$2BiCl_3 + 3H_2S = Bi_2S_3 + 6HCl.$$

Trisulphide of bismuth is less fusible than the metal itself. Heated out of access of air, it evolves sulphur, even at a very moderate temperature. Heated with access of air, it forms oxide of bismuth and sulphurous anhydride. When heated on charcoal, before the blowpipe, it is easily reduced to the metallic state, especially if a little carbonate of sodium be added. At a gentle heat, it dissolves in chlorhydric acid with evolution of sulphuretted hydrogen, in nitric acid with separation of sulphur, and in sulphuric acid with production of sulphurous anhydride. It is unaffected by alkaline hydrates and sulphydrates.

A few sulphobismuthites have been found native, of which the best defined are kobellite Pb_3BiS_3, and needle-ore $Pb_2CcuBiS_3$. Copper-bismuth-glance and nickel-bismuth-glance are double sulphides, of which the formulæ are not established.

(403) SULPHOTELLURIDE OF BISMUTH. *Sym.* Bi_2Te_2S; *p. n.* 710.—This compound constitutes the mineral known as telluric bismuth, or tetradymite. It occurs crystallized in modified rhombohedral forms. Its lustre is metallic, its colour intermediate between that of lead and tin, and its sp. gr. from 7·5 to 7·8. It fuses readily before the blowpipe, exhaling an odour of sulphur and selenium, of which last it usually contains some traces. It dissolves readily in nitric acid, with separation of sulphur. It may be regarded as an analogue of oxisulphide of antimony Sb_2S_2O.

SALTS OF BISMUTH.

(404) TRISNITRATE OF BISMUTH. *Sym.* $Bi(NO_3)_3$; *p. n.* 396.—

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This salt is usually formed by dissolving bismuth in hot nitric acid, evaporating the liquid, and setting it aside to crystallize. It occurs in transparent colourless prisms belonging to the doubly oblique prismatic system. According to Gladstone, they contain 5 atoms, but according to other observers, only $4\frac{1}{2}$ atoms of water, thus: $2Bi(NO_3)_3.9H_2O$. This formula, if reduced to a mononitric expression, would correspond with those of hydrated nitric acid and nitrate of copper, thus: $2biNO_3.3H_2O$.* The crystals dissolve completely in dilute nitric acid, but are decomposed by water with precipitation of a basic salt, and formation of a highly acid liquid. An excess of water produces a similar decomposition of the solution of the salt in dilute nitric acid. Trisnitrate of bismuth begins to be decomposed at temperatures below 100°. At 150° it is reduced to the state of mononitrate, with evolution of nitric acid; and at 260° to the state of teroxide of bismuth, with evolution of peroxide of nitrogen and oxygen. When a solution of trisnitrate of bismuth is diluted with a moderate quantity of cold water, a white silky precipitate is produced, which may be considered as hydrated orthonitrate of bismuth $Bi'''NO_4.H_2O$, or as hydrated metanitrate of bismuthyl $(BiO)'NO_3.H_2O$, or as orthonitrate of bismuthyl and hydrogen $(BiO)'H_2NO_4$. When freshly precipitated, it is somewhat freely soluble in cold water, and still more so in water containing a little nitric acid; but after a variable time, its solution becomes turbid, with deposition of an opaque white precipitate. The precipitate thus formed, or the original precipitate after some little time, is quite insoluble, and constitutes magistery of bismuth. It seems to undergo a partial decomposition by washing with water, and hence the results of its analysis are somewhat discrepant; but they all accord more or less nearly with the formula $Bi'''NO_4.H_2O$. Becker represents the washed precipitate by the formula $5Bi_2O_3,4N_2O_5.9H_2O$. Both varieties of mononitrate of bismuth lose half their water at 100°, and are converted into the compound $2Bi'''NO_4.H_2O$. Gladstone obtained the same product by heating crystallized trisnitrate of bismuth to 150°.

(405) SULPHATES OF BISMUTH.—Three of these salts have been described. The normal salt $Bi'''_2(SO_4)_3$, is made by acting upon bismuthous oxide with sulphuric acid, or by heating metallic bismuth with the strong acid. It is a white amorphous mass, soluble in dilute sulphuric acid, from which it may be obtained on evapor-

* bi = ½Bi.

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ation in needle-shaped crystals. It is decomposed by water into the insoluble basic salt, and a solution of sulphuric acid, in which some of the normal salt remains dissolved.

The basic salt, $Bi_2(SO_4)_3 . 2Bi_2O_3$, is made by heating the normal salt until it turns yellow, or by decomposing it with water. It is an insoluble white powder, becoming temporarily yellow when hot. When strongly heated, it gives off sulphurous anhydride and oxygen. It might be represented as neutral sulphate of bismuthyl: $Bi_2(SO_4)_3 . 2Bi_2O_3 = 3(BiO)_2SO_4$; but this formula probably belongs to the hydrated salt shortly to be referred to.

Acid sulphate of bismuthyl, $(BiO)'HSO_4.H_2O$, separates in small delicate needles when sulphuric acid is added to a solution of bismuthous nitrate in dilute nitric acid. It is decomposed by washing with water, leaving a hydrated neutral sulphate of bismuthyl $(BiO)'_2SO_4.2H_2O$. When heated, it evolves sulphuric acid and water, and is converted into the anhydrous basic salt.

(406) Carbonate of Bismuth.—This salt, $(BiO)'_2CO_3 . H_2O$, is formed by decomposing a solution of nitrate of bismuth in dilute nitric acid, with an alkaline carbonate. It is a white precipitate, insoluble in excess of carbonic acid. It may also be represented as an orthocarbonate of bismuthyl and hydrogen $(BiO)_2H_2CO_4$.

(407) Oxalates of Bismuth.—The normal oxalate $Bi_2'''(C_2O_4) . 3H_2O$, is obtained as a white powder, by treating bismuthous hydrate with excess of aqueous oxalic acid. Boiling water converts it into a crystalline acid oxalate of bismuthyl $(BiO)'HC_2O_4$, which last salt is decomposed at a little above 200°, with evolution of carbonic anhydride.

(408) Phosphate of Bismuth.—This compound $Bi'''PO_4$, is thrown down as a white precipitate on adding phosphate of sodium to a solution of bismuthous nitrate in dilute nitric acid. When heated, it fuses into an enamel-like mass. It is soluble in acetic and in dilute nitric acids.

§ VI. The Nitrogen Group of Elements.

(409) Nitrogen, Phosphorus, Arsenic, Antimony, Bismuth.—Each of these five elements has the property of combining with three atoms either of hydrogen or of its representatives, chlorine and ethyl, to constitute a two-volume molecule. Bismuth is not known to form a hydrogenised compound, but the first four members of the group are distinguished from all other elements by their capability of forming terhydrides. In these terhydrides,

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which are all gaseous, the three atoms or volumes of hydrogen and the one atom of nitrogen-element are condensed into the space of two volumes. Hence when two volumes of phosphamine, for instance, H_3P, are decomposed by an iron wire, heated to redness by the transmission of a galvanic current, the phosphorus is absorbed by the iron, and the original two volumes of gas are increased to three; whereas if the experiment were made with two volumes of sulphydric acid H_2S, only two volumes of hydrogen would remain after the absorption of the sulphur, and if it were made with two volumes of chlorhydric acid HCl, only one volume of hydrogen would remain after the absorption of the chlorine. Again, two volumes of ammonia H_3N, are decomposed by a succession of Rühmkorff sparks into four volumes of gas, three of hydrogen and one of nitrogen; whereas the electrolysis of water H_2O, furnishes only two volumes of hydrogen for one of oxygen, and that of chlorhydric acid HCl, only one volume of hydrogen for one of chlorine. The chemical correlations of ammonia and phosphamine are very marked, while phosphamine, arsenamine, and stibamine present the most complete analogies. They all result from, and are capable of effecting, similar reactions.

Phosphorus, arsenic, and antimony correspond in their general characters, and present a definite gradation of properties. Nitrogen seems to bear to the central members of the group, much the same relation that fluorine and oxygen bear to the other members of the first and second groups respectively. The atomic weights of phosphorus, arsenic, and antimony occur in sequence: —

P	31				
As	75	mean	=	75·33	= $\frac{226}{3}$
Sb	120				
Sum	226	mean difference	=	44?	

The atomic weight of nitrogen, or 14, is rather less than half that of phosphorus, whilst the atomic weight of bismuth is less than twice that of antimony to much the same extent; for $\frac{14\times2}{31} = \frac{210}{120\times2}$, or at least the difference only amounts to ·028. The atomic heats of phosphorus, arsenic, antimony, and bismuth are respectively 5·84, 6·10, 6·09, and 6·56, giving a mean of 6·12. But there is no obvious relation between the atomic volumes of the members of this group, that of phosphorus being 211, that of arsenic 105, that of antimony 224, and that of bismuth 270. The specific gravities of phosphorus, arsenic, antimony, and bismuth are respectively

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1·8 to 2·2, 5·6, 6·7, and 9·8. The vapour densities of phosphorus and arsenic are anomalous, being the doubles of their respective atomic weights. The metallic character is most decided in bismuth, is somewhat less marked in antimony, is scarcely acknowledged in arsenic, and vanishes in phosphorus.

Corresponding compounds of phosphorus, arsenic, antimony, and bismuth are for the most part isomorphous. The isomorphism of the phosphates and arsenates, in particular, is very complete, as illustrated by the following compounds: —

KH_2PO_4	KH_2AsO_4
$(NH_4)_2HPO_4$	$(NH_4)_2HAsO_4$
$NaNH_4HPO_4 . 4H_2O$	$NaNH_4HAsO_4 . 4H_2O$
$Na_2HPO_4 . 12H_2O$	$Na_2HAsO_4 . 12H_2O$
$Mg_2NH_4PO_4 . 6H_2O$	$Mg_2NH_4AsO_4 . 6H_2O$

The arsenious and antimonious anhydrides are isodimorphous, and arsenic is frequently substituted for antimony by an isomorphous displacement in the sulphantimonites $M_3(^{As}_{Sb})S_3$. Again, the trisulphides of antimony and bismuth are isomorphous; and antimony displaces bismuth in kobellite, needle-ore, &c. With regard to the free elements, arsenic and antimony are isomorphous with one another and paramorphous with bismuth.

The analogy in composition and properties, manifested by the similar compounds of the five elements, is most striking and complete; although the obvious properties of one set of bodies are sometimes represented by the latent properties of their analogues. The series of corresponding chlorides, oxides, and sulphides is very perfect, as shown below: —

Cl_3N	N_2O	N_2O_4	N_2S_2	P_2S_5
Cl_3P	N_2O_2	Sb_2O_4	As_2S_2	As_2S_5
Cl_3As		Bi_2O_4	Bi_2S_2	Sb_2S_5
Cl_3Sb	N_2O_3			
Cl_3Bi	P_2O_3	N_2O_5	P_2S_3	Sb_2S_2O
	As_2O_3	P_2O_5	As_2S_3	Bi_2Te_2S
Cl_5P	Sb_2O_3	As_2O_5	Sb_2S_3	
Cl_5Sb	Bi_2O_3	Sb_2O_5	Bi_2S_3	
		Bi_2O_5		

Owing to its instability, the trichloride of nitrogen has been hardly examined. The other four trichlorides are volatile bodies, yielding two-volume gaseous molecules. The boiling points of the trichlorides of phosphorus, arsenic, and antimony, namely, 74°,

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132°, and 223°, rise in regular sequence, while that of bismuth is considerably higher still. All four trichlorides are decomposed by excess of water, with exchange of chlorine for peroxide of hydrogen. The teroxides also are very uniformly gradational in their physical and chemical properties. Teroxide of nitrogen is a highly volatile liquid, that of phosphorus a very volatile solid, that of arsenic a less volatile solid, that of antimony a solid volatile only at a full red heat, and that of bismuth a comparatively fixed solid, or at any rate one that requires for its volatilization an extremely high temperature. The teroxides or anhydrides of nitrogen and phosphorus are decidedly chlorous, and form strongly acid liquids by their reactions with water. Teroxide of arsenic is but feebly chlorous, that of antimony still less so, while that of bismuth is neutral or basic. The last three teroxides are all of them capable of acting as bases, in which case they replace three atoms of metallic protoxide; or rather an atom of each of the three metals is capable of displacing three atoms of hydrogen to form a salt. From even very dilute acidulous solutions of arsenious, antimonious, and bismuthous salts, the metal of each is precipitated most completely at a boiling temperature, by the introduction of metallic copper, with the production of similar alloys.

The primary hydrides of the elements of this group, and their derivatives by substitution of halogen, metal, or alcohol-radicle, unite with oxygen or sulphur in several corresponding proportions, as we have seen, to form analogous bodies, thus: —

H_3N	H_3P	H_3As	H_3Sb	Cl_3Bi
———	Cl_3PO	HMe_2AsO_2	Et_3SbO	Et_3BiO
———	H_3PO_2	HMe_2AsO_2	———	———
HPb_2NO_3	H_3PO_3	Ag_3AsO_3	Ag_3SbS_3	H_3BiO_3
Hg_3NO_4	H_3PO_4	H_3AsO_4	Na_3SbS_4	

All the above normal, or ortho-compounds, are essentially trihydric, trichloric, trimetallic, &c.; but there also exist corresponding more or less complete series of meta-compounds which are monhydric, mono-metallic, &c., and which result from the ortho-compounds by an abstraction from them of an atom of water or sulphuretted hydrogen, or of oxygen- or sulphur-base, thus: —

Red silver	Ag_3SbS_3	—	Ag_2S	=	$AgSbS_2$	Myargyrite.
Orthophospate	KH_2PO_4	—	H_2O	=	KPO_3	Metaphosphate.

The following may be cited as examples of these meta-com-

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pounds, some of which are even more stable and better known than are the corresponding ortho-compounds: —

ClNO	ClAsO	ClBiO
KNO_2	$PbSbS_2$	$HBiO_2$
HNO_3	HPO_3	$HBiO_3$

There are also intermediate or para-compounds resulting apparently from the union of ortho- with meta-compounds. Thus we have parasulphantimonate of iron $Fe_4Sb_2S_5$, and paraphosphate of sodium $Na_4P_2O_7$, &c.

(410) The above class of meta-compounds serves to associate the members of the third group of elements with those of the first. There are indeed no compounds HN or MN, analogous to HCl or MCl; but, as already observed, there are many definite bodies that may be regarded as oxidized compounds of HN, or MN, which in their formulæ and properties correspond closely with the oxidized compounds of HCl and MCl. Thus we have

Chlorite of potassium	$KClO_2$	KNO_2	Nitrite of potassium.
Chlorate of potassium	$KClO_3$	KNO_3	Nitrate of potassium.

Again, N_2O_4 corresponds closely with Cl_2O_4, and ClNO may be looked upon as a representative of ClClO.

The members of the third group of elements are associated likewise with the members of the second by the circumstance that, although their characteristic tendency is to unite with three atoms of hydrogen or metal, yet they have also the property of uniting with two atoms of metal, &c., to form compounds analogous to those of the second group. Thus we have phosphorus-iodide I_2P, corresponding to sulphur-iodide I_2S; arsenide of nickel Ni_2As, corresponding to selenide of nickel Ni_2Se; and antimonide of zinc Zn_2Sb, corresponding to telluride of zinc Zn_2Te. Some of these compounds are isomorphous with one another; arsenide of nickel Ni_2As, with sulphide of nickel Ni_2S, for instance. Again, we have arsenides and sulphur-arsenides corresponding to bisulphides. Thus, mispickel FeAsS, is isomorphous with marcasite Fe_2S_2, while smaltine Co_2As_2, and cobalt-glance Co_2AsS, are isomorphous with common iron pyrites Fe_2S_2. Moreover, the metals arsenic and antimony are isomorphous with tellurium. Nevertheless, the bodies H_2N, or amidogen, and Me_2As, or kakodyl, are not in any respects analogous to H_2O or water, and to Me_2Se, or selenide of methyl; but bear respectively the same relations thereunto, that HO, or

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peroxide of hydrogen, bears to HCl, or chlorhydric acid. We have four typical two-volume molecules, namely HCl, H_2O, H_3N, and H_4C. If from each of these we abstract an atom of hydrogen, we obtain the one-volume radicles Cl, HO, H_2N, H_3C, which in the free state, however, must be represented as two-volume molecules, Cl_2, H_2O_2, H_4N_2, and H_6C_2, respectively.

It is interesting to contrast the parallel oxacid compounds to which chlorine, sulphur, and phosphorus respectively give origin.

Monhydric.	Dihydric.	Trihydric.
HCl	H_2S	H_3P
HClO	Cl_2SO	Cl_3PO
$HClO_2$	Cl_2SO_2	H_3PO_2
$HClO_3$	H_2SO_3	H_3PO_3
$HClO_4$	H_2SO_4	H_3PO_4

Phosphoric acid H_3PO_4, is the representative on the phosphorus series, of sulphuric acid H_2SO_4, on the sulphur series, and of perchloric acid $HClO_4$, on the chlorine series; but whereas perchloric acid contains only one atom of hydrogen, and can form only one class of salts and ethers; whereas sulphuric acid contains only two atoms of hydrogen, and can form only two classes of salts and ethers; phosphoric acid contains three atoms of hydrogen, and can form three classes of salts and ethers. One third, two thirds, or three thirds of its hydrogen may be displaced by some metal or basic radicle; or its hydrogen may be partly or wholly displaced by two or three different metals, or by two or three different radicles, or by a mixture of metals and radicles, to form complex salts, such as $EtKCuPO_4$, $H(NH_4)NaPO_4$, &c.

(411) Frequent reference has already been made to the compounds known as amides (pars. 23 and 24, 216, 222, 233). In chlorhydric acid HCl, we can replace the whole but not any fraction of the hydrogen, by some other element; in water H_2O, we can replace either one half or two halves of the hydrogen; and in ammonia H_3N, one third, or two thirds, or three thirds. If we represent ammonia by the quaternary formula shown below, the propriety of representing similarly constituted molecules on the same type is self-evident, thus:—

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N,\quad \left.\begin{matrix}K\\H\\H\end{matrix}\right\}N,\quad \left.\begin{matrix}I\\I\\H\end{matrix}\right\}N,\quad \left.\begin{matrix}Zn\\Zn\\Zn\end{matrix}\right\}N,\quad \left.\begin{matrix}H\\H\\H\end{matrix}\right\}P,\quad \left.\begin{matrix}Cu\\Cu\\Cu\end{matrix}\right\}As,\quad \left.\begin{matrix}Ag\\Ag\\Ag\end{matrix}\right\}Sb,\quad \left.\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right\}Bi,\ \&c.$$

Corresponding to every protochloride, then, we have two possible oxides, and three possible nitrides, thus:—

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$$\left.\begin{matrix}Zn\\ \end{matrix}\right\}Cl, \qquad \left.\begin{matrix}Zn\\ H\end{matrix}\right\}O, \quad \left.\begin{matrix}Zn\\ Zn\end{matrix}\right\}O, \qquad \left.\begin{matrix}Zn\\ H\\ H\end{matrix}\right\}N, \quad \left.\begin{matrix}Zn\\ Zn\\ H\end{matrix}\right\}N, \quad \left.\begin{matrix}Zn\\ Zn\\ Zn\end{matrix}\right\}N.$$

But we are in the habit of referring to the ammonia-type bodies of a much more complex nature than any of the above, when we have regard only to such of their reactions, formative or transformative, as resemble those of ammonia and of its derivatives by elementary substitution. Precisely, for instance, as we represent the compound C_2H_5Cl on the chlorhydric acid type, and the compounds C_2H_6O and $C_4H_{10}O$ on the water type, so do we represent the compounds C_2H_7N, $C_4H_{11}N$, and $C_6H_{15}N$ on the ammonia type. All these compounds are procurable by various processes, and among others, by a direct interchange of the grouping or radicle C_2H_5, for the hydrogen of the different types:—

$$\left.\begin{matrix}C_2H_5\\ \end{matrix}\right\}Cl, \qquad \left.\begin{matrix}C_2H_5\\ H\end{matrix}\right\}O, \quad \left.\begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\right\}O, \qquad \left.\begin{matrix}C_2H_5\\ H\\ H\end{matrix}\right\}N, \quad \left.\begin{matrix}C_2H_5\\ C_2H_5\\ H\end{matrix}\right\}N, \quad \left.\begin{matrix}C_2H_5\\ C_2H_5\\ C_2H_5\end{matrix}\right\}N.$$

Amides are sometimes distinguished according to the chlorous or basylous nature of the elementary or compound radicles entering into their constitution. Those with acid radicles retain the name amides; those with basic radicles receive the name amines; while those with both acid and basic radicles are called amin-amides or alkalamides. These three classes of compounds correspond respectively to chlorous oxides, such as nitric acid $H(NO_2)O$, and nitric anhydride $(NO_2)_2O$; to basic oxides, such as potassic hydrate HKO, and potassic oxide K_2O; and to neutral oxides or salts, such as nitrate of potassium $K(NO_2)O$.

Amides in which one third of the hydrogen is displaced are termed primary; those in which two thirds of the hydrogen are displaced, secondary; and those in which three thirds are displaced, tertiary. The two atoms of displaced hydrogen in some secondary amides, are represented by a diequivalent radicle to form compounds known as imides, and the three atoms of displaced nitrogen in some tertiary amides, by a triequivalent radicle to form compounds known as nitryls. Thus, we have carbimide or cyanic acid $(CO)''HN$, ethylen-phenylimine $(C_2H_4)''(C_6H_5)'N$, phosphoro-nitryl or monophosphamide $(PO)'''N$, and aceto-nitryl or cyanide of methyl $(C_2H_3)'''N$, &c.

Precisely as hydrates may be looked upon as chlorides in which an atom of chlorine is exchanged for one of eurhyzen HO, so may primary amides be looked upon as chlorides in which an atom of

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chlorine is exchanged for one of amidogen H_2N; and it is often most convenient to consider the reactions by which primary amides are formed as consisting merely in an interchange of H_2N for Cl; thus:—

$Zn.Cl$	$Zn.HO$	$Zn.H_2N.$
$(C_2H_5).Cl$	$(C_2H_5).HO$	$(C_2H_5).H_2N.$

Through a similar interchange, chloracetic acid $C_2H_3ClO_2$, for instance, becomes glycolic acid $C_2H_4O_3$ by its reaction with water or a metallic hydrate, and glycolamic acid or glycocol $C_2H_5NO_2$, by its reaction with ammonia, thus:—

$$C_2H_3ClO_2 + H.HO = C_2H_3(HO)O_2 + HCl.$$
$$C_2H_3ClO_2 + H.H_2N = C_2H_3(H_2N)O_2 + HCl.$$

Secondary amides, moreover, may in the same way be regarded as oxides in which an atom of oxygen is replaced by one of imidogen HN; diethylamine for instance $(C_2H_5)_2HN$, may be compared with ether $(C_2H_5)_2O$; but at present this mode of viewing the secondary amides offers very few practical advantages. Precisely as, by a well understood convention, we are accustomed to refer the chlorides and oxides of polyatomic radicles to multiple chlorhydric acid and water types; so do we refer certain amides of polyatomic radicles to multiple ammonia types. The compounds we have already considered which are derived from the single atom of ammonia are termed by way of distinction monamides, whilst those derived from the double atom of ammonia are termed diamides, and those from the triple atom of ammonia triamides. The polyamides, like the monamides, are divisible into amides, amines, and alkalamides, and include primary, secondary, tertiary and intermediate varieties. We may adduce the following diamides by way of illustration:—

Carbamide.	Phosphodiamide.	Phenyloxamide.	Ethylendiamine.	Diethylendiamine.	Triethylendiamine.
$(CO)''$	$(PO)'''$	$(C_2O_2)''$	$(C_2H_4)''$	$(C_2H_4)''$	$(C_2H_4)''$
H_2	H	$(C_6H_5)'H$	H_2	$(C_2H_4)''$	$(C_2H_4)''$
H_2	H_2	H_2	H_2	H_2	$(C_2H_4)''$
N_2	N_2	N_2	N_2	N_2	N_2.

We may also adduce the following triamides:—

Phosphotriamide.	Triphenylcitramide.	Cyanethine.
$(PO)'''$	$(C_6H_5O_4)'''$	$(C_3H_5)'''$
H_3	$(C_6H_5)'_3$	$(C_3H_5)'''$
H_3	H_3	$(C_3H_5)'''$
N_3	N_3	N_3.

(412) A diatomic radicle, sulphuryl for instance $(SO_2)''$ is not

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only capable, as we have seen, of displacing two atoms of hydrogen in the double molecules of chlorhydric acid, water, and ammonia, thus: —

H_2Cl_2 and $(SO_2)''Cl_2$, $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$ and $\left.\begin{matrix}(SO_2)''\\H_2\end{matrix}\right\}O_2$, $\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}N_2$ and $\left.\begin{matrix}(SO_2)''\\H_2\\H_2\end{matrix}\right\}N_2$

but it is also capable of displacing two atoms of hydrogen in the mixed chlorhydric acid-water and water-ammonia molecules, thus: —

Chlorhydro-sulphurous acid.

$$\left.\begin{matrix}H.Cl\\H\\H\end{matrix}\right\}O \text{ and } \left.\begin{matrix}(SO_2)''\\H\end{matrix}\right\}Cl\,O'$$

Sulphamic acid.

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N \text{ and } \left.\begin{matrix}H\\H\\(SO_2)''\\H\end{matrix}\right\}N$$
$$\left.\begin{matrix}H\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}\\\\\\H\end{matrix}\right\}O$$

Of course chlorhydro-sulphurous acid might be represented, and with good reason, either on the chlorhydric acid type as $(HSO_3)Cl$, or on the water type as $\left.\begin{matrix}ClSO_2\\H\end{matrix}\right\}O$, but the above more complex expression, introduced by Williamson, affords a much clearer insight into the decompositions and recompositions of the body. By referring any complex body to a simple type, we pay regard only to such of its reactions, formative or transformative, as correspond with those of the type. But when more complex decompositions have to be expressed than the typical body is capable of undergoing, then the complex body can no longer be satisfactorily represented by its simple typical formula. Every compound body may in fact be represented by a series of typical formulæ, getting more and more complicated until they terminate in a mere synoptic expression of its constituent elements, which last constitutes for every compound its most general formula. Now intermediate between these ultimate expressions, and those derived from our simple types HCl, H_2O, and H_3N, we have formulæ derived from mixed chlorhydric acid-water, chlorhydric acid-ammonia, water-ammonia, and chlorhydric acid-water-ammonia types, thus:—

$$\left.\begin{matrix}H.Cl\\H\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}H.Cl\\H\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}H\\H\\H\\H\\H\end{matrix}\right\}\begin{matrix}O\\\\N\\\\\end{matrix} \qquad \left.\begin{matrix}H.Cl\\H\\H\\H\\H\end{matrix}\right\}\begin{matrix}O\\\\N\\\\\end{matrix}$$

In these mixed types, multiples of some or all the constituent types may be substituted for the simple types above expressed.

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Benzamide furnishes us with a very good illustration of the use of formulæ derived from mixed types. It usually reacts as an ammonia, and consequently is usually represented on the ammonia type, to indicate the class of reactions of which it is susceptible. But it sometimes reacts as a hydrate, and we then represent it on the water-type. But we may readily represent it also on the mixed water-ammonia type, whereby we not only indicate its capability of undergoing both sets of reactions, but we show at a glance the possibility of its being dehydrated into benzo-nitryl or cyanide of phenyl C_7H_5N, thus:—

$$\left.\begin{matrix}(C_7H_5O)'\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}(C_7H_6N)'\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}H\\(C_7H_5)'''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$$

Indeed, with the radicle C_7H_5, a much greater variety of benzoic compounds and reactions can be expressed than is possible with the radicles C_7H_5O or C_7H_6N. At the same time, for very many bodies, including benzamide $(C_7H_5O)H_2N$, the formulæ of Gerhardt, derived each from a simple primary type, are capable of expressing all the most familiar reactions of the bodies, and are best adapted to the general requirements of chemical science.

But for the large class of compounds known as amic acids, and for their salts, the formulæ derived from the water-ammonia type are most generally applicable. The acids represent the above mixed type $\left.\begin{matrix}NH_2.H\\H\end{matrix}\right\}O$, or $\left.\begin{matrix}H_3\\H_2\end{matrix}\right\}\begin{matrix}N\\O,\end{matrix}$ in which two, three, or four atoms of hydrogen are displaced by radicle-substitution. There are no known amic acids containing only monatomic radicles, although there are many corresponding amic bases, the hydrate of tetrethylium, for instance $\left.\begin{matrix}N(C_2H_5)_4\\H\end{matrix}\right\}O$. But an amic acid is always related to some polybasic acid, and contains some polyatomic radicle. The normal amic acid of any simple polybasic acid differs from it in ultimate constitution, by containing one atom of oxygen less and one atom of hydrogen more, together with an atom of nitrogen; or, in other words, it results from its corresponding polybasic acid by an exchange of amidogen H_2N, for peroxide of hydrogen HO. The following are offered as examples:—

Sulphamic. $\left.\begin{matrix}NH_2(SO_2)''\\H\end{matrix}\right\}O$ Oxybenzamic. $\left.\begin{matrix}NH_2(C_7H_4O_2)''\\H\end{matrix}\right\}O$ Phosphamic. $\left.\begin{matrix}NH(PO)'''\\H\end{matrix}\right\}O$

Sulphanilic. $\left.\begin{matrix}NH(C_6H_5)'(SO_2)''\\H\end{matrix}\right\}O$ Ethyloxamic. $\left.\begin{matrix}NH(C_2H_5)'(C_2O_2)''\\H\end{matrix}\right\}O$ Phenylcitramic. $\left.\begin{matrix}N(C_6H_5)'(C_6H_5O_4)'''\\H\end{matrix}\right\}O$

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